FATS AND OILS
A SERIES OF MONOGRAPHS

Industrial Oil and Fat Products
Second Edition
By Alton E. Bailey

•

Fatty Acids
By Klare S. Markley

•

Melting and Solidification of Fats
By Alton E. Bailey

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Cottonseed and Cottonseed Products
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Soybeans and Soybean Products
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FATS AND OILS

A SERIES OF MONOGRAPHS ON THE CHEMISTRY AND
TECHNOLOGY OF FATS, OILS, AND RELATED SUBSTANCES
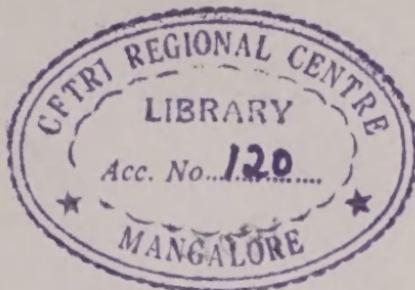
INDUSTRIAL
OIL AND FAT
PRODUCTS

*Second Completely Revised and Augmented Edition*

ALTON E. BAILEY

DIRECTOR OF RESEARCH, THE HUMKO COMPANY
MEMPHIS, TENNESSEE

1951
INTERSCIENCE PUBLISHERS, INC., NEW YORK
INTERSCIENCE PUBLISHERS LTD., LONDON

1802

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PREFACE
to the First Edition

This volume is intended to be primarily a text on oil and fat technology, hence the greater part (comprising Sections C and D) is devoted to a description and discussion of the commercially important oil and fat products and the processes used in the manufacture of these products. In two preliminary sections (A and B), the chemical and physical nature of fats and oils is briefly reviewed, and the various fatty raw materials are considered with respect to their composition, characteristics, and availability.

The rapid advance of oil and fat technology in the past few years has made it possible to include much important material not available in older books. All material, both old and new, has been treated critically, and the endeavor throughout has been to devote space to individual subjects in approximate proportion to their actual or potential importance to industry.

Although the present text has naturally been based upon the previous literature, attention should be called to the considerable amount of technical material which is published here for the first time. An attempt has been made to fill, at least partially, some of the more notable gaps in the literature of oil and fat technology. These gaps occur principally in the field of edible fats and oils, where there is a particular dearth of published information on plastic shortening agents and bakery products, and on the practical operations of refining, bleaching, deodorization, and hydrogenation. In attempting to fill these gaps the author has had recourse to his own experience, and to the advice of many friends in the industry.

In the preparation of the manuscript the author has been most fortunate in having the assistance of a number of persons who have read the individual chapters and given him the benefit of their expert advice and suggestions. For their invaluable help in this particular he is deeply indebted to Robert M. Walsh, G. S. Jamieson, K. S. Markley, George W. Irving, Jr., S. T. Bauer, F. G. Dollear, Bruce Miller, Ralph Potts, Joe Kirby, A. A. Robinson, George Carlin, H. P. Trevithick, A. S. Richardson, J. J. Vollertsen, L. E. Osmer, Henry A. Gardner, G. G. Sward, Francis Scofield, L. B. Parsons, Warren H. Goss, and Arthur J. Lewis. Sincere thanks are also expressed to Mr. R. O. Feuge, who prepared most of the original drawings for the illustrations, to Mr. C. H. Billett for assistance in pre-

paring photographs for many of the illustrations, to Miss Dorothy Becke-
meyer for checking the literature references, to Mr. Robert H. McKinney
for the loan of photographs for the chapter on bakery products, to the
editors of *Oil and Soap* and *Industrial and Engineering Chemistry* for
permission to reproduce illustrative material, to the various manufacturers
of processing equipment who supplied photographs and drawings for
illustrations, and to all those responsible for the typing and checking of
the manuscript.

A. E. BAILEY

New Orleans, Louisiana
May 16, 1944

PREFACE
to the Second Edition

The six years that have elapsed since the appearance of the first edition
have comprised a period of remarkable productivity in fats and oils re-
search, as well as one of notable technological progress. As a consequence,
it has been more difficult than before (and it may well be regarded as
more presumptuous) for one author to endeavor to treat all phases of the
oil and fat industry and to do justice to its complexities within the con-
fines of a single volume. Nevertheless, the attempt has again been made.

Although the book has been largely rewritten, its plan and scope are
essentially those of the first edition, except that the rather lengthy chap-
ter on "Production and Consumption" has been omitted (partly because
of the inadequacy of recent world-wide statistical data, and partly to con-
serve space), and the subject of "Handling, Storage, and Grading," pre-
viously included under "Extraction," has been expanded into a separate
chapter. Again, the author has written from detailed personal experience
only in dealing with certain aspects of edible fats and their utilization,
and has had to rely in large measure upon the literature and upon outside
help in covering other subjects. For the kind assistance of his friends and
colleagues, who are too numerous to mention, he wishes to express his
sincere thanks.

A. E. BAILEY

Memphis, Tennessee
April, 1951

CONTENTS

C. INDUSTRIAL UTILIZATION OF FATS AND OILS

A. THE NATURE OF FATS AND OILS

STRUCTURE AND COMPOSITION OF FATS AND OILS[1]

Fats and oils are substances of plant or animal origin which consist predominantly of triglyceryl esters of the fatty acids, or *triglycerides*. In general, the term "fat" is used in reference to materials which are solid, or more properly, semisolid, at ordinary temperatures, whereas the term "oils" is reserved for those which are liquid under the same conditions. However, it is obvious that no rigid distinction can be made between the two, and here the common practice will be followed of using the terms interchangeably, except where a distinction between solid and liquid materials is important.

A. Glycerides

1. TRIGLYCERIDES

From the structural standpoint, a *triglyceride* may be considered to be formed by the condensation of one molecule of glycerol with three molecules of fatty acids to yield three molecules of water and one molecule of a triglyceride.

$$
\begin{array}{cccccc}
\text{H} & & & & & \text{H} \\
| & & & & & | \\
\text{H—C—OH} & \text{H—OOC—R}_1 & \text{HOH} & & \text{H—C—OOC—R}_1 \\
| & & & & & | \\
\text{H—C—OH} & + \;\; \text{H—OOC—R}_2 & \longrightarrow & \text{HOH} & + & \text{H—C—OOC—R}_2 \\
| & & & & & | \\
\text{H—C—OH} & \text{H—OOC—R}_3 & \text{HOH} & & \text{H—C—OOC—R}_3 \\
| & & & & & | \\
\text{H} & & & & & \text{H} \\
\text{Glycerol} & \text{Fatty acids} & \text{Water} & & \text{Triglyceride}
\end{array}
$$
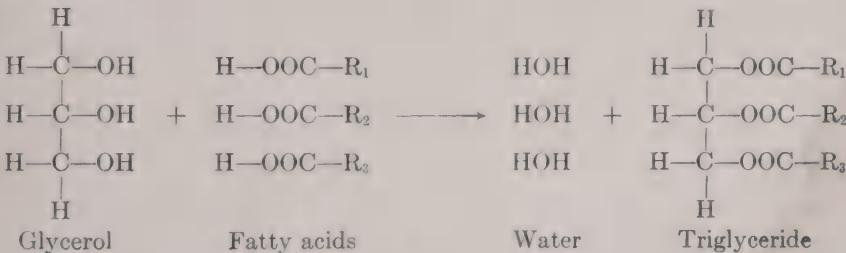
If the three fatty acids are identical, the product is a *simple triglyceride*; if they are different, it is a *mixed triglyceride*. Each mixed triglyceride containing three different acid radicals has three different isomeric forms,

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[1] GENERAL REFERENCES: T. P. Hilditch, *The Chemical Constitution of Natural Fats,* 2nd ed., Chapman & Hall, London, 1947. G. S. Jamieson, *Vegetable Fats and Oils,* 2nd ed., Reinhold, New York, 1943. J. A. Lovern, *The Composition of the Depot Fats of Aquatic Animals,* Dept. Sci. Ind. Res., Food Investigation Special Rept. No. 51, H. M. Stationery Office, London, 1942. K. S. Markley, *Fatty Acids,* Interscience, New York, 1947. G. B. Martinenghi, *Chimica e Tecnologia degli Oli, Grassi e Derivati,* 2nd ed., Ulrico Hoepli, Milan, 1948. A. W. Ralston, *Fatty Acids and Their Derivatives,* Wiley, New York, 1948. H. Schönfeld, ed., *Chemie u. Technologie der Fette u. Fettprodukte,* Vol. I, Springer, Vienna, 1936.

according to which fatty acid is in the inside (β) position in the mole
and which acids are consequently in the outside (a and a') positi
Each mixed triglyceride containing two different fatty acids similarly
two isomeric forms.

H	H	H
H—C—palmitic acid	H—C—oleic acid	H—C—oleic acid
H—C—oleic acid	H—C—palmitic acid	H—C—palmitic acid
H—C—stearic acid	H—C—stearic acid	H—C—palmitic acid
H	H	H
β-Oleopalmitostearin	β-Palmitooleostearin	a-Oleodipalmitin
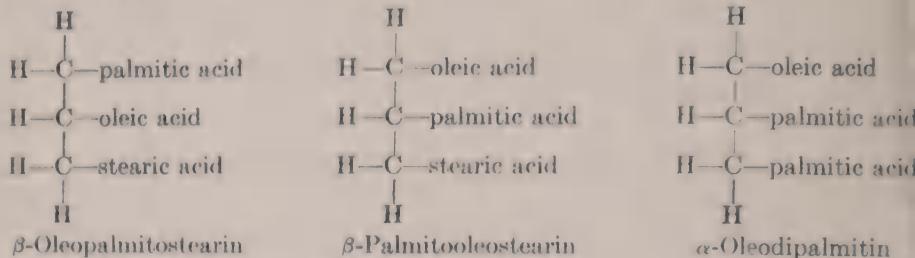
2. MONO- AND DIGLYCERIDES

Monoglycerides and *diglycerides* contain only one and two fatty a
radicals, respectively, and consequently have free hydroxyl groups. T
occur naturally in appreciable quantities only in fats which have bec
partially hydrolyzed, but are easily prepared synthetically and have
portant industrial uses.

Under conditions which are favorable to acyl migration the fatty a
radicals in mono- and diglycerides tend to move to the outside positi
in the molecule; hence manufactured products apparently contain o
a-monoglycerides and a,a'-diglycerides.[3]

—C—stearic acid	—C—oleic acid
—C—OH	C—OH
—C—OH	—C—oleic acid
a-Monostearin	a,a'-Diolein
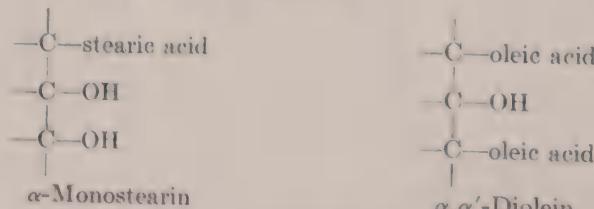
Appreciable amounts of diglycerides, and probably also monoglycerid
are present in low-grade fats which have undergone considerable hydrol
sis as a result of enzyme action in the parent vegetable or animal tissue
It is probable that traces of these compounds occur in all commercial fa

3. STRUCTURE OF NATURAL GLYCERIDES

The glycerides of fats are in general highly mixed. Simple triglycerid
appear to be the exception rather than the rule; they occur for the mo

[3] The a-, β-, and a'- positions are referred to by some writers as the "1-," "2
and "3-" positions, respectively.
[3] See, for example, J. Ross, A. C. Bell, C. J. Arrowsmith, and A. I. Gebhart, (
& Soap, 23, 257–259 (1946). This is in accord with the observation of T. H. Clar
and G. Stegeman, J. Am. Chem. Soc., 62, 1815–1817 (1940), that a-monoglycerid
have the lower heat of combustion, and hence are thermodynamically more stable.
[4] See, for example, E. Schlenker and J. Gnaedinger, J. Am. Oil Chem. Soc.,
239–240 (1947); H. H. Mueller and E. K. Holt, ibid., 25. 305–307 (1948).

part in the relatively few fats which contain a single fatty acid in such preponderant amounts that the formation of this class of glycerides is unavoidable.

A large part of present knowledge of glyceride structure is derived from an extensive series of investigations on many different fats and oils carried out over a period of years by Hilditch and co-workers.[1] These investigations have led to the deduction of a "rule of even distribution" governing the composition of natural fats. According to this rule, each of the individual fatty acids of a fat tends to be apportioned as evenly as is possible among the different glyceride molecules. Consequently, fatty acids which are present in minor quantities are inclined to appear but singly in the glycerides. Acids which comprise more than one-third of the total fatty acids will generally appear in nearly all the glyceride molecules, and an acid must be present to the extent of at least two-thirds of the total fatty acids to form any considerable amount of simple glycerides.

The fats which appear to follow most closely the principle of even distribution are those derived from vegetable seeds. Vegetable fruit coat fats are inclined to deviate somewhat from the rule, and animal fats exhibit quite marked deviations. The latter are notable, in particular, for a tendency to have their saturated acids closely grouped, to form considerable proportions of fully saturated glycerides. Thus, for example, beef fat may contain 12 to 20% of fully saturated glycerides, even though its content of saturated acids is not greater than 50 to 60%.

It has been suggested[5] that in animal fats the distribution of saturated and unsaturated fatty acids may conform to a pattern of random distribution among the glyceride molecules (see page 834), and the fact that the melting point of animal fats is not greatly altered by interesterification to produce random distribution has been cited[6] as evidence in favor of this view. It appears much more likely, however, as pointed out by Hilditch,[7] that the failure of interesterification to alter the melting point (or the content of fully saturated triglycerides) is purely fortuitous, and that extreme deviation from even distribution in animal fats is the result of hydrogenation within the animal tissues of fats originally synthesized approximately according to an even distribution pattern. Actually, published estimates of the proportions of disaturated, monosaturated, and triunsaturated glycerides in animal fats differ greatly from those predicted upon the basis of random distribution; further evidence that such distribution does not occur is provided by the fact that interesterification markedly alters the consistency of animal fats at various temperatures

[5] H. E. Longenecker, *Chem. Revs.*, *29*, 201–224 (1941). R. W. Riemenschneider, E. Luddy, M. L. Swain, and W. C. Ault, *Oil & Soap*, *23*, 276–282 (1946).
[6] K. F. Mattil and F. A. Norris, *Science*, *105*, 257–259 (1947); *J. Am. Oil Chem. Soc.*, *24*, 274–275 (1947).
[7] T. P. Hilditch, *J. Am. Oil Chem. Soc.*, *26*, 41–45 (1949).

below their final melting points, even though the melting point itself may undergo no substantial change (see, for example, Table 130, page 828).

Doerschuk and Daubert[8] have published an elaborate analysis of the glyceride structure of corn oil—based upon a fractional crystallization technique—which purports to show a modified pattern of random distribution. Their conclusions are open to very serious objection, however, since they are founded on the scarcely tenable thesis that the solubilities of a large number of mixed glycerides stand in the same relative order as their iodine values rather than their melting points.

The analytical data collected in Table 1 show characteristic glyceride compositions of vegetable oils containing different proportions of saturated and unsaturated fatty acids, and also illustrate the difference between vegetable and animal fats of similar fatty acid composition. It is to be emphasized that the so-called rule of even distribution only describes a

TABLE 1

ESTIMATED GLYCERIDE COMPOSITIONS OF REPRESENTATIVE VEGETABLE AND ANIMAL FATS

Fat	Fatty acids, mol. %		Glycerides,[a] mol. %			
	Sat.	Unsat.	SSS	SSU	SUU	UUU
Mutton tallow[b]	60.8	39.2	28	29	40	3
Cocoa butter[c]	59.8	40.2	2	77	21	0
Beef tallow[d]	57.9	42.1	15	46	37	2
Palm oil[e]	52.5	47.5	8	54	32	6
Lard, European[f]	42.4	57.6	5	39–32	46–60	8–3
Lard, American[d]	37.4	62.6	2	26	55	17
Cottonseed oil[e,g]	28.4	71.6	0	13	59	28
Peanut oil[e,h]	19.2	80.8	0	1	56	43
Olive oil[e,i]	15.1	84.9	0	0	45	55

[a] SSS = trisaturated, SSU = disaturated, SUU = monosaturated, UUU = triunsaturated.

[b] T. P. Hilditch and R. K. Shrivastava, *J. Am. Oil Chem. Soc.*, *26*, 1–4 (1949).

[c] T. P. Hilditch and W. J. Stainsby, *J. Soc. Chem. Ind.*, *55*, 95–101T (1936).

[d] R. W. Riemenschneider, F. A. Luddy, M. L. Swain, and W. C. Ault, *Oil & Soap*, *23*, 276–282 (1946).

[e] T. P. Hilditch and M. L. Meara, *J. Soc. Chem. Ind.*, *61*, 117–125 (1942). T. P. Hilditch and L. Maddison, *ibid.*, *59*, 67–71T (1940).

[f] T. P. Hilditch and W. H. Pedelty, *Biochem. J.*, *34*, 971–979 (1940).

[g] T. P. Hilditch and L. Maddison, *J. Soc. Chem. Ind.*, *59*, 162–168 (1940).

[h] B. G. Gunde and T. P. Hilditch, *J. Soc. Chem. Ind.*, *59*, 47–53 (1940).

[i] T. P. Hilditch and L. Maddison, *J. Soc. Chem. Ind.*, *60*, 258–262 (1941).

trend, and that it is by no means followed with sufficient exactness to permit the glyceride composition of a fat to be calculated from its known composition in terms of component fatty acids. The data of numerous workers show that seed oils may contain appreciable proportions of trisaturated glycerides without more than two-thirds of their fatty acids being saturated, or appreciable proportions of triunsaturated glycerides

[8] A. P. Doerschuk and B. F. Daubert, *J. Am. Oil Chem. Soc.*, *25*, 425–433 (1948).

without two-thirds of their fatty acids being unsaturated, and that the relative proportions of disaturated and monosaturated acids may differ considerably from those corresponding to strictly even distribution.

If a natural mixed triglyceride contains one fatty acid that differs from the other two acids—with respect to either unsaturation or chain length— the odd acid appears generally to occupy the inner or β position in the molecule. Thus, in a number of fats, including cocoa butter, cottonseed oil, and lard, Meara[9] has found such glycerides as β-oleodistearin, β-oleo-dipalmitin, β-palmitodiolein, β-palmitooleostearin, and β-palmitooleo-linolein, to the exclusion of the corresponding α isomers. However, there are exceptions to this rule. In palm oil, [9a] α- and β- oleodipalmitins occur in approximately equal proportions, and there are more α- than β-palmito-dioleins. The palmitodistearin of beef tallow is lower melting than that of lard, and hence presumably is largely the α isomer.[10]

B. Fatty Acids

The molecular weight of the glyceryl portion (C_3H_5) of a triglyceride molecule is 41. The combined molecular weight of the fatty acid radicals (R.COO) comprising the remainder of the molecule will vary with different oils from about 650 to 970. Thus the fatty acids contribute from 94 to 96% of the total weight of the molecule.

$$
\begin{array}{c}
H \\
| \\
\textit{Molecular} \qquad H-C-OOC.R_1 \qquad \textit{Molecular} \\
\textit{weight} \qquad \quad | \qquad\qquad\qquad \textit{weight} \\
41 \qquad\qquad H-C-OOC.R_2 \qquad 650\ to\ 970 \\
| \\
H-C-OOC.R_3 \\
| \\
H
\end{array}
$$
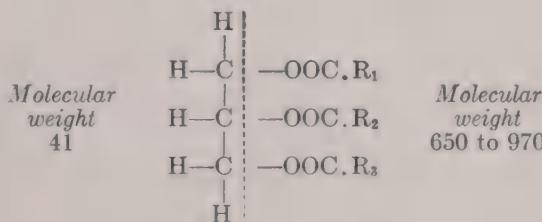
Because of their preponderant weight in the glyceride molecules, and also because they comprise the reactive portion of the molecules, the fatty acids greatly influence the character of the glycerides. Consequently, the chemistry of fats and oils is to a very large extent the chemistry of their constituent fatty acids.

The naturally occurring fatty acids are in general normal, monobasic aliphatic compounds, consisting almost invariably of a single carboxyl group attached to the end of a straight hydrocarbon chain. With a single exception (isovaleric acid), the fatty acids which are found in nature contain an even number of carbon atoms.[11] The individual acids differ

[9] M. L. Meara, *J. Chem. Soc.*, *1945*, 22–24; *1947*, 773–775; *1949*, 2154–2157.
[9a] M. L. Meara, *J. Chem. Soc.*, *1948*, 722–726.
[10] A. Börner, R. Limprich, R. Krönig, and J. Kuhlmann, *Z. Untersuch. Nahr.-ienussm.*, *26*, 559–618 (1913).
[11] Actually, in one sense isovaleric acid constitutes no exception to the general rule, s this acid has an even number of carbon atoms in its main carbon chain. It may be onsidered a C_4 acid with a methyl group substituted for one hydrogen atom.

from one another primarily in the number of carbon atoms in their chains, and the number and position of the ethylenic linkages or double bonds between the carbon atoms.

Those fatty acids in which all carbon atoms in the chain are linked with not less than two hydrogen atoms, and which thus contain no double bonds, are termed *saturated*. The fatty acids which contain double bonds are termed *unsaturated*. The degree of unsaturation of an oil depends upon the average number of double bonds in its fatty acids.

<pre>
    H   H   H   H   H   H   H   H
    | | | | | | | |
  --C---C---C---C--   --C---C===C---C--
    | | | | | |
    H   H   H   H   H   H
</pre>
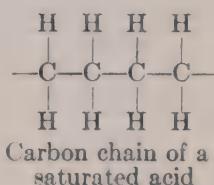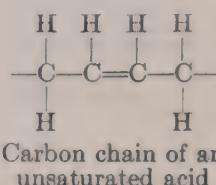
<div align="center">
Carbon chain of a   Carbon chain of an
saturated acid   unsaturated acid
</div>

The more common fatty acids are usually referred to by name, as lauric, palmitic, oleic, etc. The Geneva nomenclature provides a scheme for applying to each acid a name definitive of its chemical composition. Under this system, the number of carbon atoms is indicated by a Greek prefix. Thus, for example, acids of 12, 14, 16, and 18 carbon atoms take the respective prefixes, dodec-, tetradec-, hexadec-, and octadec-. Saturated acids are distinguished by the suffix, -anoic, and unsaturated acids by the suffix, -enoic. Palmitic acid, for example, is designated as hexadecanoic acid.

The number of double bonds in the fatty acids is indicated by a suitable prefix; thus, linoleic acid, with two double bonds, is a dienoic acid, while linolenic acid, with three double bonds, is a trienoic acid. The position of the double bonds is indicated by prefixing the numbers of the carbon atoms between which the double bonds occur, or, according to the practice of some writers, the numbers of the carbon atoms *preceding* the double bonds. In numbering the carbon atoms, the one in the carboxyl group is designated as number one, and the remainder are numbered consecutively to the end of the chain.

<pre>
  18 17 16 15 14 13 12 11 10   9   8   7   6   5   4   3   2   1
   H   H   H   H   H   H   H   H   H   H   H   H   H   H   H   H   H
   | | | | | | | | | | | | | | | | |
 H-C---C---C---C---C---C===C---C---C===C---C---C---C---C---C---C---C--COOH
   | | | | | | | | | | | | |
   H   H   H   H   H   H   H   H   H   H   H   H   H
</pre>

<div align="center">
9:10, 12:13 octadecadienoic (linoleic) acid
</div>
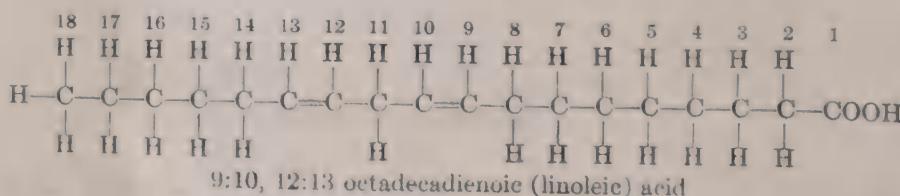
Polyunsaturated fatty acids of the *nonconjugated* type, in which double bonds in the carbon chain are always separated by at least two single bonds, are to be distinguished from *conjugated* acids, in which single and double bonds alternate between certain carbon atoms.

Nonconjugated fatty acid chain   Conjugated fatty acid chain
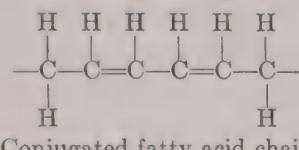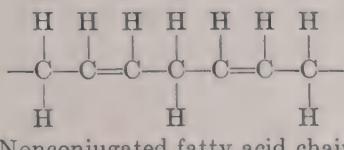
The reactivity of an unsaturated fatty acid is determined by the position as well as the number of its double bonds. The juxtaposition of two double bonds with a single methylene (CH_2) group intervening confers much greater reactivity than the presence of two more widely separated bonds (see page 706). Conjugated acids and their esters are notable for the extreme readiness with which they undergo certain reactions, *e.g.*, polymerization.

Monounsaturated fatty acids are capable of existing in either the *cis*- or the *trans*-form, according to the mode of juncture of the two portions of the molecule on either side of the double bond. A *trans*-linkage produces less irregularity in the straight chain structure, hence of the two, the *trans*-forms are higher melting, and generally also less reactive. The number of possible *cis-trans* isomers increases rapidly with an increase in the number of double bonds. A diethenoid acid may theoretically exist in four forms: *cis-cis, cis-trans, trans-cis, and trans-trans*; a triethenoid acid in eight, etc. With but very few exceptions, *e.g.*, vaccenic acid, naturally occurring fatty acids appear to be *cis*-isomers. However, *cis*-acids may be converted to *trans*-isomers in the course of certain processing treatments.

The average degree of unsaturation of a fat or mixture of fatty acids is measured by the *iodine value;* the average molecular weight is measured by the *saponification value* or *saponification equivalent*, or their counterparts, the *neutralization value* or *neutralization equivalent*. Further discussion of these important analytical values will be found in Chapter II.

In addition to the ordinary fatty acids described above, there are a limited number of natural fatty acids with peculiarities of structure, such as triple bonds, substituted hydroxyl or ketone groups, or closed carbon rings. These acids will be discussed individually in a later section.

1. SATURATED FATTY ACIDS

The saturated fatty acids occurring in fats and oils are listed in Table 2, together with their boiling points and melting points, and the melting points of the corresponding simple triglycerides. Other properties and characteristics of these acids will be reviewed in succeeding chapters devoted to the reactions and physical properties of fats and fatty acids.

At a given temperature, the vapor pressure of fatty acids decreases regularly with increase in the chain length. The difference in boiling point between adjacent members of the series is sufficient to permit efficient separation of mixtures by means of fractional distillation.

The melting points of the saturated acids exhibit a progressive increase as the carbon chain is lengthened. Differences in the melting points of the acids are reflected in the melting points of the simple glycerides, as shown in Table 2, and also in those of mixed triglycerides. Thus, milk fats and vegetable fats of the coconut oil type, which contain large proportions of C_6 to C_{12} acids, have much lower melting points than fats with an equivalent degree of unsaturation that are composed substantially of C_{16} and C_{18} acids.

TABLE 2

BOILING POINTS OF SATURATED FATTY ACIDS AND MELTING POINTS OF ACIDS AND
CORRESPONDING SIMPLE TRIGLYCERIDES

Acid	Boiling point, °C. at 16 mm.	Melting point of acid, °C.	Melting point of triglyceride, °C.[a]
Butyric	163	−8	—
	(at 760 mm.)		
Caproic	107	−3.4	—
Caprylic	135	16.7	—
Capric	159	31.6	31.5
Lauric	182	44.2	46.4
Myristic	202	54.4	57.0
Palmitic	222	62.9	65.5
Stearic	240	69.6	73.1
Arachidic	—	75.4	—
Behenic	—	80.0	—
Lignoceric	—	84.2	—

[a] Melting point of the highest melting, most stable crystal modification.

Butyric acid is found only in milk fats, to the amount of 2–4% by weight of the total fatty acids. *Caproic* acid also occurs in milk fats (1–3%) and in traces in coconut and palm kernel oils. *Caprylic* acid constitutes about 2–8% of the total fatty acids of the latter oils, and about 1–4% of the acids of the more common milk fats. *Capric* acid likewise is a characteristic component of milk fats and *Palmae* seed oils, occurring to the amount of 1–8% in each. It is almost or entirely lacking in most other fats; however, its richest known source is, peculiarly, the seed oil of the elm tree, where it apparently may comprise as much as 50% of the total acids.[12]

Lauric acid derives its name from the *Lauraceae*, some members of which are reported to have over 90% of lauric acid in the mixed fatty acids from the seed oil. However, the richest common source of this acid consists of coconut and palm kernel oils, which contain 40–50%. Lauric acid is found in small amounts, *i.e.*, 2–6%, in milk fats. *Myristic* acid is a

[12] M. A. Pavlenko, *Chem. Rev. Fett- u. Harz-Ind.*, **19**, 43 (1912). H. A. Schuette and C. M. Lunde, *Oil & Soap*, **13**, 12–13 (1936).

minor constituent (2% or less) of many common seed oils, fruit coat oils, and animal fats. It occurs in milk fats to the extent of 8–12%, and in coconut and palm kernel oils to 15–30%. It is a major component of seed fats of the *Myristicaceae* family (nutmeg butter, ucuhuba butter, etc.), where it may constitute 70–80% of the total fatty acids.

While fatty acids with a molecular weight less than that of myristic acid are not commonly considered to be constituents of ordinary seed oils, it is to be noted that traces of such acids may well occur undetected in many oils. Wikoff, Kaplan, and Berman[13] have reported the presence of very small amounts of caprylic and lauric acids in peanut oil.

Palmitic acid is the most widely distributed of the saturated fatty acids. It occurs in practically all animal and vegetable fats to the extent of at least 6–8%, and is a major constituent of lard, tallow, palm oil, and cocoa butter, and other vegetable butters. In Chinese vegetable tallow it comprises 60–70% of the total fatty acids. *Stearic* acid is also widely distributed. Most vegetable oils contain in the neighborhood of 1–3%. Lard, tallow, and cocoa butter contain approximately 8%, 17%, and 35%, respectively. *Arachidic, behenic,* or *lignoceric* acids do not occur in quantity in any of the more common fats or oils, although milk fats and many seed oils contain traces of these acids, and peanut oil contains 1–3% of each. Certain Oriental fats (Rambutan tallow, Pulasan fat, Macassar nut fat) contain as much as 20–35% of arachidic acid. Lignoceric acid to the amount of 25.5% has been reported in the seed fat of the East Indian tree *Adenanthera pavonina*.[14] Behenic acid was first found in the oil from the seed of the tropical behen or ben tree (*Moringa oleifera*); Jamieson[15] has reported a content of 6.3% in a sample of this oil originating in Haiti.

Saturated acids higher than lignoceric apparently do not occur in natural glycerides.

2. Unsaturated Fatty Acids

The unsaturated acids which occur in fats and oils are known with much less certainty than the saturated acids because of the relative difficulty of isolating and characterizing these compounds. The highly unsaturated fatty acids with four or more double bonds, which are found principally in marine oils, are particularly difficult subjects for study, because of the readiness with which they isomerize or polymerize under the influence of heat or chemical reagents. At the present time, therefore, the naturally occurring fatty acids present a somewhat ill-defined picture. In general,

[13] H. L. Wikoff, J. M. Kaplan, and A. L. Berman, *J. Biol. Chem., 153,* 227–235 (1944).
[14] S. M. Mudbidri, P. R. Ayyar, and H. E. Watson, *J. Indian Inst. Sci., A11,* 173–180 (1928).
[15] G. S. Jamieson, *Oil & Soap, 16,* 173–174 (1939).

those of a limited degree of unsaturation may be said to have been more
less clearly identified, but much confusion and uncertainty exists concer
ing the more unsaturated members.

In the following section, the individual unsaturated acids will be me
tioned first in the order of their degree of unsaturation, and second in a
cending order of their molecular weights. Discussion will be confined
the ordinary acids containing straight hydrocarbon chains; the relative
few unsaturated acids of abnormal structure will be considered later (pa
18), as will acids which are not found in nature, but may be prepar
synthetically, or produced by processing treatments commonly applied
natural oils or their fatty acids.

(a) *Monoethenoid Acids*

A decenoic acid (10 carbon atoms with 1 double bond) has been found
traces in butterfat.[16] Its double bond is in the 9:10 position. Anoth
4:5, decenoic acid is said to occur in small quantities in a few commercial
unimportant seed fats.[17]

Traces of 9:10-dodecenoic or *lauroleic* acid (12 C atoms, 1 double bon
have been reported in butterfat,[18] and the corresponding 4:5 acid occu
in the seed fats mentioned in the preceding paragraph. There are trac
of a dodecenoic acid of uncertain configuration in sperm whale and po
poise oils.[19] The head oil of the sperm whale contains 4% of a dodeceno
acid of undetermined structure.[20]

Butterfat contains in the neighborhood of 1% of 9:10-tetradecenoic
myristoleic acid (14 C atoms, 1 double bond).[16] Small amounts of th
4:5 acid occur in the seed fats mentioned above. The 9:10 acid is found
traces in most marine oils, and a 5:6-dodecenoic acid is found in conside
able quantity in sperm whale head oil[20,21] and in the blubber fat of th
sperm whale and other toothed whales.[1,19] There are probably traces
tetradecenoic acid in many land animal fats.

Palmitoleic, 9:10-hexadecenoic acid (16 C atoms, 1 double bond)
present in traces, *i.e.*, about 1% or less, in many vegetable oils, includin
olive, palm, cottonseed, peanut, and soybean oils.[21a] It is present in mil
fats, and in lard, tallow, etc., in slightly greater amounts (*e.g.*, 2–3%
and is found in the fats of birds, reptiles, and amphibia in still greate

[16] A. W. Bosworth and J. B. Brown, *J. Biol. Chem.*, *103*, 115–134 (1933).
[17] Y. Toyama, *J. Soc. Chem. Ind. Japan*, *40*, 285–289B (1937). S. Komori and
Ueno, *Bull. Chem. Soc. Japan, 12*, 433–435 (1937).
[18] T. P. Hilditch and H. E. Longenecker, *J. Biol. Chem.*, *122*. 497–506 (1937).
[19] Y. Toyama and T. Tsuchiya, *Bull. Chem. Soc. Japan, 10*, 563–570 (1935).
[20] T. P. Hilditch and J. A. Lovern, *J. Soc. Chem. Ind., 47*, 105–111T (1928).
[21] M. Tsujimoto, *J. Soc. Chem. Ind. Japan, 30*, 10 (1927).
[21a] R. E. Bridge and T. P. Hilditch, *J. Chem. Soc.. 1950*, 2396–2399, have recentl
found 20.4% palmitoleic acid in the fatty acids of oil from seed from the Australia
evergreen tree, *Macadamia ternifolia.*

quantity (6–15%). In the fats of most whales and fishes, including those from which whale and fish oils are obtained commercially, palmitoleic acid comprises from 10 to 20% of the total fatty acids. Hilditch[1] has pointed out that in animal fats there is a progressive decrease in the proportion of this acid corresponding to the evolutionary development of the animal. Only the 9:10 form of hexadecenoic acid has thus far been reported in nature.

Oleic acid, 9:10-octadecenoic acid (18 C atoms, 1 double bond), is the most widely distributed of all fatty acids. It occurs in some quantity in all fats and oils. In most liquid vegetable oils it is a major component, accounting for 20% or more of the total fatty acids, and in many important oils, including olive oil, palm oil, peanut oil, sesame oil, corn oil, and sunflowerseed oil, it is the principal acid. In milk fats, lard, and tallows it is also the chief acid; and it occurs in considerable quantity in virtually all animal fats whether of land or marine origin. It is only a minor component of the highly saturated lauric acid oils and a few other oils, such as castor oil and tung oil, which consist predominantly of a single glyceride.

Two other natural octadecenoic acids appear to have been positively identified. These are *petroselenic* acid, which contains a double bond in the 6:7 position, and vaccenic acid, in which there is a *trans*-bond in the 11:12 position. Petroselenic acid is peculiar to parsley seed oil and other commercially unimportant seed oils of the *Umbelliferae* and *Araliaceae*, in which it is a major component. *Vaccenic* acid occurs in traces (0.05–0.20%) in lard, beef, and mutton fats, and to the amount of 0.5–0.7% in butterfat.[22] It apparently does not occur in vegetable oils.

Millican and Brown[23] have reported experimental results which suggest the presence of octadecenoic acids other than ordinary oleic acid not only in many animal fats, but also in soybean and rapeseed oils.

Gadoleic acid,[24,25] 9:10-eicosenoic acid (20 C atoms, 1 double bond) is a minor component of many, if not virtually all, marine oils. Eicosenoic acids apparently do not occur in most vegetable oils or land animal fats, although de la Mare and Shorland[26] have reported the presence of traces of such an acid in lard.

Erucic acid, 13:14-docosenoic acid (22 C atoms, 1 double bond), is found only in oil from seeds of the *Cruciferae*. It comprises in the neighborhood of 50% of the total fatty acids of both rapeseed and mustardseed oils.

[22] S. H. Bertram, *Biochem. Z.*, *197*, 433–441 (1928). J. Grossfeld and A. Simmer, *Z. Untersuch. Lebensm.*, *59*, 237–258 (1930). E. Brouwer and M. C. E. Jonker-Scheffner, *Rec. trav. chim.*, *65*, 408–412 (1946). R. P. Geyer, H. Nath, V. H. Barki, C. A. Elvehjem, and E. B. Hart, *J. Biol. Chem.*, *169*, 227–228 (1947).
[23] R. C. Millican and J. B. Brown, *J. Biol. Chem.*, *154*, 437–450 (1944).
[24] M. Takano, *J. Soc. Chem. Ind. Japan*, *36*, 1317 (1933).
[25] Y. Toyama and T. Tsuchiya, *J. Soc. Chem. Ind. Japan*, *37*, 14B, 17B (1934).
[26] P. B. D. de la Mare and F. B. Shorland, *Analyst*, *69*, 337–339 (1944); *Nature*, *155*, 48–49 (1945).

Cetoleic acid[27] 11:12-docosenoic acid, like gadoleic acid, is a minor component of many marine oils.

Selacholeic acid,[28] 15:16-tetracosenoic acid (24 C atoms, 1 double bond) appears to occur in traces in a number of fish oils.

With the single exception of vaccenic acid, all of the above monoethenoid acids appear to have the *cis*-form.

(b) Di- and Triethenoid Acids

In vegetable oils, oleic acid is invariably associated with *linoleic* acid, 9:10, 12:13 octadecadienoic acid (18 C atoms, 2 double bonds). In the less unsaturated vegetable oils, linoleic acid is generally subordinate in amount to oleic acid; but in the more unsaturated oils, such as soybean oil, linseed oil, perilla oil, etc., there is more linoleic than oleic acid. It is ordinarily assumed that linoleic acid has the *cis-cis*-form.

Because of its failure to yield petroleum ether-insoluble bromides, the octadecadienoic acid present in butterfat and in certain animal body fats, such as beef and mutton tallows, has in the past generally been assumed to be different from the linoleic acid of vegetable oils. However, late investigations[29,30] have revealed that insoluble bromides are not obtained from the mixed fatty acids of butterfat or tallow only because linoleic acid is present in small amounts relative to oleic acid. Insoluble tetrabromides similar to those from vegetable oils are obtained when the octadecadienoic acids are concentrated by fractional crystallization.

Hilditch and co-workers have reported 2.3% of a docosadienoic acid (22 C atoms, 2 double bonds) in rapeseed oil,[31] and *ca.* 5% of a conjugated (2:3, 4:5) decadienoic acid in stillingia oil.[31a]

A hexadecatrienoic acid (16 C atoms, 3 double bonds) is believed to occur commonly in small amounts in marine oils and has been reported in rape leaf oil.[32] According to Toyama and Tsuchiya,[33] the double bonds of the hexadecatrienoic acid in Japanese sardine oil are probably in the 6:7, 10:11, 14:15 positions. This acid has been given the name, *hiragonic*.

Linolenic acid, 9:10, 12:13, 15:16-octadecatrienoic acid (18 C atoms, 3 double bonds), occurs in varying amount in some of the more unsaturated vegetable oils. In linseed and perilla oils, it is the principal fatty acid, constituting 40% or more of the total acids. An octadecatrienoic acid which presumably is linolenic acid is found in mare's milk fat[34] and in at

[27] Y. Toyama, *J. Soc. Chem. Ind. Japan*, *30*, 597–602 (1927).
[28] M. Tsujimoto, *J. Soc. Chem. Ind. Japan*, *30*, 868–873 (1927).
[29] H. B. Knight, E. F. Jordan, Jr., and D. Swern, *J. Biol. Chem.*, *164*, 477–482 (1946).
[30] M. F. White and J. B. Brown, *J. Am. Oil Chem. Soc.*, *26*, 385–388 (1949).
[31] T. P. Hilditch, P. A. Laurent, and M. L. Meara, *J. Soc. Chem. Ind.*, *66*, 19–22 (1947).
[31a] A. Crossley and T. P. Hilditch, *J. Chem. Soc.*, *1949*, 3353–3357.
[32] F. B. Shorland, *Nature, 156*, 269–270 (1945).
[33] Y. Toyama and T. Tsuchiya, *Bull. Chem. Soc. Japan*, *10*, 192–199 (1935).
[34] T. P. Hilditch and H. Jasperson, *Biochem. J.*, *38*, 443–447 (1944).

least some land animal fats—tallow contains *ca.* 0.5%[35] and horse fat 5–6%. It is possible that this acid may also occur in small amounts in marine animal fats. However, Tsuchiya[36] has stated that an octadecatrienoic acid occurring in sardine oil has its double bonds at the 6:7, 10:11, 14:15, or 6:7, 10:11, 13:14, or 6:7, 9:10, 13:14 positions. The only known nonconjugated natural octadecatrienoic acid other than linolenic acid is 6:7, 9:10, 12:13 acid which is confined to the seeds of a single plant, the night candle plant, *Oenothara biennis*.[37]

Elaeostearic acid, 9:10, 11:12, 13:14-octadecatrienoic acid, is the conjugated isomer of linolenic acid. It forms about 85% of the total fatty acids of tung oil, and is found also in certain other seed oils of the *Rosaceae*, *Euphorbiaceae*, and *Cucurbitaceae*, none of which are of present commercial importance.

When long exposed to light or certain other isomerizing influences the natural "alpha" form of elaeostearic acid is transformed to a higher melting "beta" form, with consequent solidification of its glycerides. The solvent extraction of tung oil produces glycerides of the beta form of the acid, which may, however, be permanently converted to those of liquid form by being heated to a high temperature.[38] Differences in the two forms apparently arise from *cis-trans* isomerism.[38a]

Two other octadecatrienoic acids have been isolated which are believed to be geometric isomers of elaeostearic acid. These are *punicic* acid, which occurs in pomegranate seed oil[39] and *trichosanic* acid which is found in the seed oil of the East Indian plant, *Trichosanthes cucumeroides*.[40]

The positive identification of both octadecadienoic and octadecatrienoic acids has been rendered difficult by the circumstance that, in the past, the sole available method has been the formation and separation of their insoluble bromine addition compounds. This method has never been very satisfactory. As mentioned above, the octadecadienoic acid of butterfat and tallows does not form an insoluble bromide unless concentrated, and in fact both linoleic and linolenic acids fail to give quantitative or closely predictable yields of insoluble bromides, because of solubilization effects, and possibly because these acids partially isomerize during the bromination process. It may be mentioned in this connection that the terms alpha

[35] See the following: H. B. Knight, E. F. Jordan, Jr., and D. Swern, *J. Biol. Chem.*, *164*, 477–482 (1946); B. A. Brice, M. L. Swain, B. B. Schaeffer, and W. C. Ault, *Oil & Soap*, *22*, 219–224 (1945); and B. A. Brice and M. L. Swain, *J. Optical Soc. Am.*, *35*, 532–544 (1945).

[36] T. Tsuchiya, *J. Chem. Soc. Japan*, *63*, 650–653 (1942).

[37] A. Eibner, L. Widenmeyer, and E. Schild, *Chem. Umschau Fette Öle Wachse Harze*, *34*, 312–320 (1927). See also J. P. Riley, *J. Chem. Soc.*, *1949*, 2728–2731.

[38] W. G. Rose, A. F. Freeman, and R. S. McKinney, *Ind. Eng. Chem.*, *34*, 612–614 (1942).

[38a] R. S. Morrell and W. R. Davis, *Trans. Faraday Soc.*, *32*, 209–219 (1936).

[39] E. H. Farmer and F. A. van den Heuvel, *J. Chem. Soc.*, *1936*, 1809–1811.

[40] Y. Toyama and T. Tsuchiya, *J. Soc. Chem. Ind. Japan*, *38*, 182–185B (1935). H. P. Kaufmann, J. Baltes, and J. Büter, *Ber.*, *70*, 2535B (1937).

or beta applied to linoleic or linolenic acids have no precise structural significance, but are used merely to designate the forms which yield solid and liquid bromides, respectively.[41]

The recently developed spectral methods for fatty acid analysis are very sensitive to traces of conjugated acids or acids whose double bonds are separated by no more than three carbon atoms, and hence can be conjugated by alkali isomerization. At present the interpretation of such analyses is complicated by the fact that slight oxidation of fats gives rise to conjugation which is not characteristic of the original material. It appears not unlikely, however, that the application of these methods will eventually show that the occurrence of the more highly unsaturated fatty acids is more widespread than has heretofore been suspected. The low-temperature fractional crystallization technique of Brown and associates[42] may also be expected to assist in the detection and identification of new unsaturated acids.

(c) Polyethenoid Acids

The single known vegetable oil fatty acid with more than three double bonds is *parinaric* acid, 9:10, 11:12, 13:14, 15:16-octadecatetraenoic acid (18 C atoms, 4 double bonds), which has been found in the seed oil of *Parinarium laurinum*.[43]

A 4:5, 8:9, 12:13, 15:16-octadecatetraenoic (*moroctic*) acid has been reported in minor amounts in Japanese sardine oil[44] and the same acid or similar acids are believed to be found generally in marine oils.

Both lard[45] and beef tallow[46] contain traces of *arachidonic* acid, eicosatetraenoic acid (20 C atoms, 4 double bonds). The double bonds of arachidonic acid are believed to be in the 5:6, 8:9, 11:12, and 14:15 positions.[47] According to various observations of Hilditch and co-

[41] For detailed information concerning the isomerism of linoleic and linolenic acids and their bromo- and hydroxy-derivatives, the reader is referred to the following publications: B. H. Nicolet and H. L. Cox, *J. Am. Chem. Soc.*, 44, 144–152 (1922); Y. Inoue and B. Suzuki, *Proc. Imp. Acad. Tokyo*, 7, 15–18 (1931); T. Maruyama and B. Suzuki, *ibid.*, 7, 379 (1931); T. Maruyama, *J. Soc. Chem. Ind. Japan*, 54, 1082–1087 (1933); J. W. McCutcheon, *Can. J. Research*, B16, 158–175 (1938); T. G. Green and T. P. Hilditch, *Biochem. J.*, 29, 1552–1563 (1935); R. W. Riemenschneider, D. H. Wheeler, and C. E. Sando, *J. Biol. Chem.*, 127, 391–402 (1939); J. P. Kass and G. O. Burr, *J. Am. Chem. Soc.*, 61, 1062–1066 (1939); T. P. Hilditch and H. Jasperson, *J. Soc. Chem. Ind.*, 58, 233–241 (1939). A summary of present knowledge of the subject is presented by T. P. Hilditch (see footnote 1, page 3).

[42] J. B. Brown and G. G. Stoner, *J. Am. Chem. Soc.*, 59, 3–6 (1937). J. B. Brown and J. Frankel, *ibid.*, 60, 54–56 (1938). G. Y. Shinowara and J. B. Brown, *ibid.*, 60, 2734–2738 (1938).

[43] E. H. Farmer and E. Sunderland, *J. Chem. Soc.*, 1935, 759–761. H. P. Kaufmann, J. Baltes, and S. Funke, *Fette u. Seifen*, 45, 302–304 (1938).

[44] Y. Toyama and T. Tsuchiya, *Bull. Chem. Soc. Japan*, 10, 192–199 (1935).

[45] J. B. Brown and E. M. Deck, *J. Am. Chem. Soc.*, 52, 1135–1138 (1930).

[46] J. B. Brown and C. C. Sheldon, *J. Am. Chem. Soc.*, 56, 2149–2151 (1934).

[47] C. L. Arcus and I. Smedley-Maclean, *Biochem. J.*, 37, 1–6 (1943).

workers,[48] the highly unsaturated fatty acid fraction of these fats also includes a C_{22} acid, the combined content of unsaturated C_{20} and C_{22} acids amounting to as much as 0.5% in the case of beef fat and 2.1% in the case of lard. Arachidonic acid and other highly unsaturated C_{20} and C_{22} acids are also found in traces in butterfat.

An eicosatetraenoic acid (20 C atoms, 4 double bonds) and an eicosapentaenoic acid (20 C atoms, 5 double bonds) have been detected in Japanese sardine oil.[49] The double bonds in these acids have been tentatively assigned to the 4:5, 8:9, 12:13, and 16:17, and the 4:5, 8:9, 12:13, 15:16, and 18:19 positions, respectively. These acids appear to be components of most marine oils.

A docosapentaenoic acid (22 C atoms, 5 double bonds) and a docosahexaenoic acid (22 C atoms, 6 double bonds) are recognized as major components of most marine oils. The name *clupanodonic* is loosely applied to both these acids. Toyama and Tsuchiya[50] have suggested that the double bonds of these acids are in the 4:5, 8:9, 12:13, 15:16, and 19:20 positions in the case of the pentaethenoid acid, and in either the 4:5, 8:9, 12:13, 15:16, 18:19, and 21:22, or the 4:5, 8:9, 11:12, 14:15, 17:18, and 20:21 positions in the hexaethenoid acid. Farmer and van den Heuvel[51] have expressed the opinion that the docosapentaenoic acid found by these workers is actually a heat-degradation product of docosahexaenoic acid, produced during fractional distillation of the mixed methyl esters of the oil. However, more recently Toyama[52] has reported that the docosapentaenoic acid may also be isolated by the fractional crystallization of its sodium soaps from acetone.

Highly unsaturated C_{24} acids appear to occur in only small amounts in most marine oils, although Brocklesby and co-workers[53] have reported such an acid in quantity in pilchard oil. A tetracosapentaenoic acid (24 C atoms, 5 double bonds) has been found in fish oil by Ueno and Iwai,[54] and a tetracosahexaenoic acid (24 C atoms, 6 double bonds), with double bonds probably in the 4:5, 8:9, 12:13, 15:16, 18:19, and 21:22 positions has been reported by Toyama and Tsuchiya.[55] These acids have been given the respective names *scoliodonic* and *nisinic*.

The occurrence in certain fish oils of traces of hexacosapentaenoic acid

[48] A. Banks and T. P. Hilditch, *Biochem. J., 26*, 298–308 (1932); H. K. Dean and T. P. Hilditch, *ibid., 27*, 1950–1956 (1933). T. P. Hilditch and H. E. Longenecker, *ibid., 81*, 1805–1819 (1937).
[49] Y. Toyama and T. Tsuchiya, *Bull. Chem. Soc. Japan, 10*, 296–300 (1935).
[50] Y. Toyama and T. Tsuchiya, *Bull. Chem. Soc. Japan, 10*, 441–453, 539–543 (1935).
[51] E. H. Farmer and F. A. van den Heuvel, *J. Soc. Chem. Ind., 57*, 24–31T (1938).
[52] Y. Toyama, *J. Chem. Soc. Japan, 64*, 41–43 (1942).
[53] H. N. Brocklesby and K. F. Harding, *J. Fisheries Research Board Can., 4*, 59–62 (1938).
[54] S. Ueno and M. Iwai, *J. Soc. Chem. Ind. Japan, 37*, 251–255B (1934).
[55] Y. Toyama and T. Tsuchiya, *Bull. Chem. Soc. Japan, 10*, 539–543 (1935).

(26 C atoms, 5 double bonds), and hexacosahexaenoic acid (26 C atoms, 6 double bonds) has been reported.[56]

3. Fatty Acids of Unusual Structure

A fatty acid of low molecular weight constituting a major component of dolphin and porpoise oils was identified by André[57] as *isovaleric* acid, $(CH_3)_2CH.CH_2.COOH$. Isovaleric acid is the sole natural fatty acid thus far discovered with an odd number of carbon atoms, and is also notable for its branched chain structure.

Tariric acid is a straight chain C_{18} acid with an acetylenic linkage or a triple bond between the 6th and 7th carbon atoms. It does not occur in and well-known fat or oil, apparently being confined to seed fat of the Central and South American genus, *Picramnia*. According to Steger and van Loon,[58] the fat of *P. tariri* contains 89.8% of this acid.

A 6:7, 9:10 C_{18} acid with one double bond and one triple bond has been reported by Steger and van Loon as a major component of the seed fat of *Ongokea gore*.[59] The relative positions of the double and triple bonds in this acid were not determined.

Ricinoleic acid, 12-hydroxy 9:10-octadecenoic acid, is similar to oleic acid except that it has an hydroxyl group substituted for a hydrogen atom at the 12th carbon atom. It occurs to the extent of about 80 to 85% of the total fatty acids in castor oil, and is responsible for the several unique properties of this oil. There are a few plants related to the castor plant which apparently yield seed oils containing this acid, but none of the oils are produced commercially.

A dihydroxystearic acid of unknown configuration has been reported by several investigators[60] as a minor or trace component of castor oil. Dihydroxystearic acid has also been reported in traces in butterfat.

Licanic acid occurs to the extent of about 70 to 75% of the total fatty acids in oiticica oil, from *Licania rigida*, and Mexican oiticicia or cacahuanache oil, [61] from *Licania arborea*. Licanic acid has been shown by Brown and Farmer[62] to be 4-keto 9:10, 11:12, 13:14-octadecatrienoic acid:

$$CH_3(CH_2)_3.CH=CH—CH=CH—CH=CH.(CH_2)_4.CO.(CH_2)_2COOH,$$
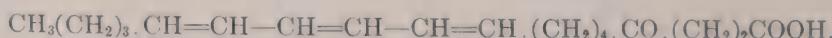
hence is identical with elaeostearic acid but for the substitution of an

[56] S. Ueno and C. Yonese, *Bull. Chem. Soc. Japan*, *11*, 437–442 (1936). S. Ueno and M. Iwai, *ibid.*, *11*, 643–649 (1936).
[57] E. André, *Bull. soc. chem.*, *35*, 857–868 (1924).
[58] A. Steger and J. van Loon, *Rec. trav. chim.*, *52*, 593–600 (1933).
[59] A. Steger and J. van Loon, *Fette u. Seifen*, *44*, 243 (1937).
[60] P. Panjutin and M. Rapoport, *Chem. Umschau Gebiete Fette Öle, Wachse Härze*, *37*, 130–135 (1930). A Eibner and H. Münzing (*Chem. Abstracts*, *19*, 3027), H. P. Kaufmann and H. Bornhardt, *Fette u. Seifen*, *46*, 444–446 (1939).
[61] W. G. Rose and G. S. Jamieson, *Oil & Soap*, *20*, 227–231 (1943).
[62] W. B. Brown and E. H. Farmer, *Biochem. J.*, *29*, 631–639 (1935).

oxygen atom for two hydrogen atoms to form a keto group at the 4th carbon atom. Licanic acid is similar to elaeostearic acid in its tendency to isomerize to a higher melting isomer, or "beta" form.

Chaulmoogric acid is a C_{18} monethenoid acid characterized by a closed five-membered carbon ring at the end of the carbon chain.[63]

$$
\begin{array}{c}
\text{H}_2 \\
\text{C} \\
\text{H}_2\text{C} \qquad \text{CH}.(\text{CH}_2)_{12}.\text{COOH} \\
\text{HC}\!\!=\!\!=\!\!\text{CH}
\end{array}
$$
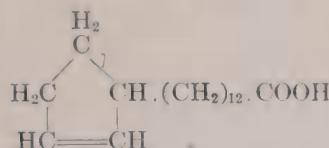
Hydnocarpic acid is similar to chaulmoogric acid, except that it is a C_{16} acid[63]; *gorlic* acid differs from chaulmoogric acid in having a double bond between the 6th and 7th carbon atoms. These three cyclic acids are confined to chaulmoogra oil and other seed oils of the *Flacourtiaceae*. All are optically active.

4. ARTIFICIAL FATTY ACIDS

Manufactured oil and fat products may in certain cases contain fatty acids which are not found in nature but are developed intentionally or unintentionally during processing treatments. Some of the more important of these acids will be briefly mentioned.

Elaidic acid is the *trans*-form of oleic acid. It is usually formed in the laboratory by the treatment of oleic acid with oxides of nitrogen, but can also be produced by heating oleic acid or its esters in the presence of sulfur, selenium, etc.

A variety of "iso-oleic" acids is formed during the catalytic hydrogenation of fats and oils. Some of these apparently consist of elaidic acid. Others are 12:13 monoethenoid acids produced by the hydrogenation of linoleic acid at the 9:10 double bond, or monoethenoid acids in which the double bond is in various positions other than the normal 9:10 position due to the wandering of double bonds from concurrent hydrogenation and dehydrogenation or other causes. Isomerization may follow double bond migration or hydrogenation at the 12:13 linkage, to produce monoethenoid *trans*-isomers other than elaidic acid. All the *trans*-isomers have melting points substantially above that of normal oleic acid, and possibly some of the *cis*-isomers are also higher melting. The degree to which high melting "iso-oleic" acids are formed has a great influence upon the melting point and consistency of hydrogenated fats (see Chapter XVII).

Comparatively little is known regarding the polyethenoid isomers formed in fats by hydrogenation. However, it is certain that such fatty acids are produced in quantity. The work of Lemon,[64] followed by that of

[63] See R. L. Shriner and R. Adams, *J. Am. Chem. Soc.*, **47**, 2727–2739 (1925).
[64] H. W. Lemon, *Can. J. Research*, **F22**, 191–198 (1944).

Mattil,[65] Daubert and Filer,[66] and Bailey and Fisher[67] has shown that the linolenic acid in soybean or linseed oil readily hydrogenates at the middle double bond to produce a 9:10, 15:16 isomer of linoleic acid. It is notable that this acid reacts more like oleic acid than linoleic acid with respect to both hydrogenation and oxidation, because of the wide degree of separation of its double bonds. Lund[68] has reported comparable isomers containing both two and three double bonds, from the hydrogenation of whale oil. Mattil[65] and also Daubert and Filer[66] have pointed out that hydrogenation may be productive of appreciable quantities of conjugated acids in oils, as well as other isomers in which double bonds have migrated to more widely separated positions. It can scarcely be doubted that *trans*-isomers also occur among the polyethenoid acids of hydrogenated oils.[68a]

Recently applied processes for improvement of the drying properties of oils have made a variety of polyethenoid isomers available. In the commercial dehydration of castor oil a conjugated 9:10, 11:12-octadecadienoic acid unknown in nature is produced (see page 433). The alkali isomerization of soybean and linseed oils has been reported[69] to yield three isomeric 10:11, 12:13 acids melting at 8°, 45°, and 57°C., respectively. The "pseudo-elaeostearic" acid (m.p., 79°C.) produced by this process is believed[70] to be a 10:11, 12:13, 14:15 acid having either a *trans-*, *trans-*, *trans-* or a *trans-*, *cis-*, *trans-*-structure.

Some slight degree of shifting of double bonds to produce conjugated acids or other isomers of natural fatty acids is the usual accompaniment of bleaching by adsorption and probably also of other processes commonly applied to edible oils. Elaidic acid and other isomers of oleic acid are produced in considerable quantities during the commercial sulfonation of fats and oils. Presumably sulfonation also causes isomerization of linoleic and other polyethenoid acids.

C. Nonglyceride Components of Fats and Oils

The fats and oils of commerce all contain small amounts of various substances other than glycerides.[71] Some of these are completely or substantially removed from the crude oils in the process of refining, and hence do not appear in most manufactured products. Of those which persist

[65] K. F. Mattil, *Oil & Soap*, *22*, 213–215 (1945).
[66] B. F. Daubert and L. J. Filer, Jr., *Oil & Soap*, *22*, 299–302 (1945).
[67] A. E. Bailey and G. S. Fisher, *Oil & Soap*, *23*, 14–18 (1946).
[68] J. Lund, *Fette u. Seifen*, *48*, 36–65 (1941).
[68a] See H. W. Lemon and C. K. Cross, *Can. J. Research*, *B27*, 610–615 (1949).
[69] J. D. Von Mikusch, *J. Am. Chem. Soc.*, *64*, 1580–1582 (1942). J. P. Kass, *paper presented at 103rd Meeting, American Chemical Society.*
[70] J. P. Kass and G. O. Burr, *J. Am. Chem. Soc.*, *61*, 3292–3294 (1939).
[71] For a comprehensive treatment of the minor components of fats and oils, see H. Schönfeld, ed., *Chemie und Technologie der Fette und Fettprodukte*, Vol. I, Springer, Vienna, 1936.

through refining treatment, some are without pronounced flavor, odor, or color, and are relatively inert from a chemical standpoint. These may be considered of minor importance, since their presence is neither objectionable nor desirable, insofar as most of the uses of the oils are concerned. However, certain other components, particularly those which have antioxygenic properties, or are strongly flavored or highly colored, may considerably affect the character of the oil, even though they be present in no more than traces. In the following section, the various nonglyceride components will be considered from the standpoint of their practical significance, rather than grouped and discussed on the basis of their chemical constitution.

1. Substances Occurring Principally in Crude Oils

In the case of most fats and oils, the greater part of the nonglyceride portion is removed by hydration or combination with alkali in the course of ordinary refining. The amount of removable nonglyceride substances other than fatty acids varies considerably. It is highest in certain seed oils, particularly in cottonseed, corn, and soybean oils, where it may constitute as much as 2 to 3% of the crude oil. Other seed oils, for example, peanut oil and coconut oil, contain comparatively little of such materials, as do the common fruit pulp oils (olive oil and palm oil). Animal fats such as lard and edible tallow, which are derived from more or less pure fatty tissues, are very low in impurities of this class, although this may not be the case with fish oils, low-grade tallows or greases, or other animal fats rendered from entire carcasses or other stock containing much nonfatty tissue.

The materials commonly removed (or largely removed) in refining may be broadly described as consisting of phosphatides, carbohydrates, and carbohydrate derivatives, protein fragments, and various resinous and mucilaginous materials of uncertain identity. In addition, alkali refining removes any free fatty acids resulting from partial hydrolysis of the oil, and effects a partial removal of sterols, carotenoid pigments, etc.

(a) Phosphatides

Phosphatides, which are associated with fats and oils in many plant and animal tissues, consist of a polyhydric alcohol (usually, but not always, glycerol) which is esterified with fatty acids and also with phosphoric acid. The phosphoric acid is, in turn, combined with a basic nitrogen-containing compound.

Two common phosphatides, *lecithin* and *cephalin*, may be considered triglycerides in which one fatty acid radical has been replaced with phosphoric acid. In lecithins the phosphoric acid is further esterified with

choline. In cephalins, the phosphoric acid is similarly esterified with cola-
mine (hydroxyethylamine).

$$
\begin{array}{l}
\quad\quad\; H \\
\quad\quad\; | \\
H\!-\!C\!-\!OOC.R_1 \\
\quad\quad\; | \\
H\!-\!C\!-\!OOC.R_2 \quad O \\
\quad\quad\; | \quad\quad\quad\quad\quad \diagup\!\diagup \\
H\!-\!C\!-\!\!-\!\!-\!O\!-\!P\!-\!O\!-\!CH_2CH_2N(CH_3)_3 \\
\quad\quad\; | \quad\quad\quad\quad\;\; \diagdown \\
\quad\quad\; H \quad\quad\quad\quad\quad O\!-\!\!-\!\!-\!\!-\!\!-\! \\
\end{array}
$$

<div align="center">Lecithin</div>

$$
\begin{array}{l}
\quad\quad\; H \\
\quad\quad\; | \\
H\!-\!C\!-\!OOC.R_1 \\
\quad\quad\; | \\
H\!-\!C\!-\!OOC.R_2 \quad O \\
\quad\quad\; | \quad\quad\quad\quad\quad \diagup\!\diagup \\
H\!-\!C\!-\!\!-\!\!-\!O\!-\!P\!-\!O\!-\!CH_2CH_2NH_2 \\
\quad\quad\; | \quad\quad\quad\quad\;\; \diagdown \\
\quad\quad\; H \quad\quad\quad\quad\quad OH \\
\end{array}
$$

<div align="center">Cephalin</div>
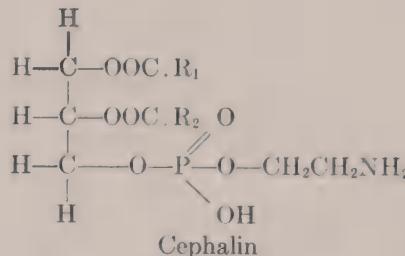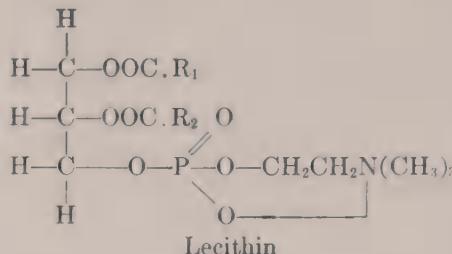
In another apparently common type of vegetable oil phosphatide, the
so-called *lipositols*,[72] the alcohol component is not glycerol, but the cyclic
alcohol inositol, $C_6H_6(OH)_6$. Esterified with the alcohol, or otherwise
combined, are fatty acids, phosphoric acid, ethanolamine tartrate, and
galactose. According to Scholfield *et al.*,[73] soybean oil phosphatides con-
sist of approximately 29% lecithins, 31% cephalins, and 40% inositol
phosphatides. There are also inositol phosphatides in cottonseed oil,[74]
and in corn oil.[74a]

By treatment with alcohol, the mixed phosphatides of vegetable oils
may be separated into an alcohol-soluble fraction consisting largely of
lecithins, and an alcohol-insoluble fraction consisting largely of cephalins
and inositol phosphatides. The analytical data of Scholfield and associ-
ates[73,74a] on fractions of soybean and corn oil phosphatides are given in
Table 2A. By countercurrent distribution between 95% methanol and
hexane, these workers were able to show that the inositol phosphatides in
soybean and corn oil are of two different types. In the case of corn oil,
but not in that of soybean oil phosphatides, most of the sugars associated
with inositol were concentrated in the hexane-soluble material. Hence,
there are evidently inositol phosphatides other than the galactose-con-
taining "lipositols".

[72] D. W. Woolley, *J. Biol. Chem., 147*, 581–591 (1943).
[73] C. R. Scholfield, H. J. Dutton, F. W. Tanner, Jr., and J. C. Cowan. *J. Am. Oil
Chem. Soc., 25*. 368–372 (1948).
[74] H. S. Olcott, *Science, 100*, 226–227 (1944).
[74a] C. R. Scholfield, T. A. McGuire, and H. J. Dutton. *J. Am. Oil Chem. Soc., 27*.
352–355 (1950).

TABLE 2A

ANALYSIS OF SOYBEAN AND CORN OIL PHOSPHATIDES[a]

Analysis	From soybean oil			From corn oil		
	Total phosphatides	Alcohol-soluble fraction	Alcohol-insoluble fraction	Total phosphatides	Alcohol-soluble fraction	Alcohol-insoluble fraction
Total nitrogen, %	1.24	1.65	0.79	1.30	1.90	1.10
Choline nitrogen, %	0.42	0.81	nil	0.39	0.85	0.098
Phosphorus, %	3.37	3.54	3.30	3.10	2.93	3.25
Sugars (as galactose), %	3.96	2.38	5.15	3.7	1.78	5.61
Inositol, %	4.18	0.26	11.3	4.27	0.14	8.0

[a] C. R. Scholfield, H. J. Dutton, F. W. Tanner, Jr., and J. C. Cowan, *J. Am. Oil Chem. Soc.*, *25*, 368–372 (1948). C. R. Scholfield, T. A. McGuire, and H. J. Dutton, *ibid.*, *27*, 352–355 (1950).

In the case of vegetable oils, the fatty acids occurring in the phosphatides and the glycerides appear to be the same, except for certain highly unsaturated C_{20} and C_{22} acids which appear only in the phosphatides. However, the proportions of the different acids in the two may be quite different. The fatty acid compositions of the alcohol-soluble (lecithin) and alcohol-insoluble (cephalin) fractions of soybean and rapeseed phosphatides, as determined by Hilditch and Pedelty,[75] are given in Table 3.

TABLE 3

FATTY ACID COMPOSITION OF SOYBEAN AND RAPESEED OIL PHOSPHATIDES

Fatty acid	Soybean		Rapeseed	
	Alcohol-insoluble, %[a]	Alcohol-soluble, %[a]	Alcohol-soluble, %[b]	Alcohol-insoluble, %[c]
Myristic.............	—	—	—	0.8
Palmitic.............	11.7	17.3	15.8	8.3
Stearic..............	4.0	—	6.3	—
Arachidic...........	1.4	—	0.0	—
Hexadecenoic........	8.6	5.5	—	2.1
Oleic...............	5.5	19.0[d]	13.0	22.4
Linoleic............	63.3[e]	53.0[f]	62.9	42.2
Linolenic...........	—	3.7	2.0	Trace
C_{26} unsaturated.......	5.5	1.5	—	22.7
Behenic.............	—	—	—	1.5

[a] T. P. Hilditch and W. H. Pedelty, *Biochem. J.*, *31*, 1964–1972 (1937).
[b] M. H. Thornton, C. S. Johnson, and M. A. Ewan, *Oil & Soap*, *21*, 85–87 (1944).
[c] Alcohol-soluble fraction was similar to alcohol-insoluble fraction.
[d] Probably higher than true value, due to oxidation of sample.
[e] Possibly including linolenic acid not exceeding 4% of total acids.
[f] Probably lower than true value, due to oxidation of sample.

A more recent analysis of the fatty acids from the alcohol-soluble (lecithin) fraction of soybean oil, by Thornton and associates,[76] also appears

[75] T. P. Hilditch and W. H. Pedelty, *Biochem. J.*, *31*, 1964–1972 (1937).
[76] M. H. Thornton, C. S. Johnson, and M. A. Ewan, *Oil & Soap*, *21*, 85–87 (1944).

in Table 3. Analyses of the fatty acids from the total phosphatides of peanut and linseed oils, as reported by Hilditch and Zaky,[77] are:

TABLE 4

FATTY ACID COMPOSITION OF PHOSPHATIDES FROM COTTONSEED, SUNFLOWER, PEANUT, AND LINSEED OILS[a]

Fatty acid	Cottonseed, %	Sunflower, %	Peanut, %	Linseed, %
Palmitic	17.3	14.7	16.2	11.3
Stearic	7.3	5.1	2.8	10.6
Arachidic	2.8	9.5	—	—
Saturated: C_{20}, C_{22}, C_{24}	—	—	4.6	—
Saturated: C_{26}	—	—	2.5	—
Hexadecenoic	1.5	—	—	3.5
Oleic	20.3	19.3	47.1	33.6
Linoleic	44.4	45.9	22.7	20.4
Unsaturated: C_{20}, C_{22}	6.4	5.5	4.1	3.2

[a] T. P. Hilditch and Y. A. H. Zaky, *Biochem. J.*, *36*, 815–821 (1942).

Phosphatides usually occur to the extent of 1 to 2% in freshly extracted soybean or corn oils, although in the crude oils of commerce the greater part of the phosphatides often has been removed by water washing of the oil. They are present in somewhat lesser amounts in other common seed oils, *e.g.*, 0.7–0.9% in crude cottonseed oil, 0.3–0.4% in crude (African) peanut oil. The phosphatide content of most animal fats is very low (Table 5). The total phosphorus content of most well-refined vegetable oils is of the order of 0.00005–0.0001%,[78] which corresponds to about 0.002–0.004% phosphatides.

TABLE 5

PHOSPHATIDE CONTENT OF VARIOUS CRUDE FATS AND OILS[a]

	Phosphatide content, %
Soybean oil	1.1–3.2 (usually *ca.* 1.8%)
Wheat oil	0.08–2.0
Butterfat, up to	1.4
Rice oil	0.5
Linseed oil	0.3
Sesame oil	0.1
Rapeseed oil	0.1
Beef fat, up to	0.07
Lard, up to	0.05
Mutton fat	0.01

[a] H. P. Kaufmann, *Fette u. Seifen*, *48*, 53–59 (1941).

Although both phosphorus and nitrogen contents of oils are commonly attributed to the presence of phosphatides, this is not altogether justifi-

[77] T. P. Hilditch and Y. A. H. Zaky, *Biochem. J.*, *36*, 815–821 (1942).
[78] M. Mattikow, *J. Am. Oil Chem. Soc.*, *25*, 200–203 (1948).

able, particularly in the case of refined oils. Von Fellenberg[79] has reported that most of the phosphorus in rapeseed oils is removed by alkali refining, but that the nitrogen content is reduced only slightly. Thornton and Kraybill[80] have noted that the nitrogen in soybean oils is evidently not all in the form of phosphatides, since adsorption refining removes phosphorus almost completely from such oils, but leaves approximately one-third of the nitrogen.

(b) Other Compounds

Raffinose and pentosans were found by Jamieson and Baughman[81] in considerable quantity in settlings from crude cottonseed oil. Carbohydrates in both free and combined forms appear to be generally associated with phosphatides in vegetable oils, and some workers are of the opinion that chemical combination may exist between the two. McKinney, Jamieson, and Holton[82] detected what was believed to be a β-glucoside-lecithin complex in soybean oil phosphatides. However, the existence of such compounds is denied by Rewald[83] who was apparently able to effect a quantitative separation of phosphatides from carbohydrates by treatment with suitable selective solvents. A glucose-phytosterol complex (phytosteroline) was isolated by Jamieson and Baughman[81] from cottonseed oil. As stated above, galactose appears to be a constituent of "lipositol."

Certain protein degradation products are sufficiently soluble or dispersible in oil to appear in appreciable quantities in some fats and oils. Their amount corresponds to the extent to which hydrolytic decomposition has occurred in the proteins of the seed or animal tissue from which the oil is derived, and hence is greatest in oil from damaged materials. Although listed here as constituents of crude oils, some of these are not entirely removed by alkali refining (see succeeding section on Pigments, page 28). Both proteoses and peptones were found by Jamieson and Baughman[81] to occur in crude cottonseed oil.

2. REFINED OIL CONSTITUENTS OF MINOR SIGNIFICANCE

(a) Sterols

Sterols are characteristic components of all natural oils and fats, comprising in most cases the greater part of the unsaponifiable matter.[84]

[79] T. von Fellenberg, *Mitt. Lebensm. Hyg.*, *36*, 355–359 (1945).
[80] M. H. Thornton and H. R. Kraybill, *Ind. Eng. Chem.*, *34*, 625–628 (1942).
[81] G. S. Jamieson and W. F. Baughman, *J. Oil & Fat Ind.*, *3*, 347–355 (1926).
[82] R. S. McKinney, G. S. Jamieson and W. B. Holton, *Oil & Soap*, *14*, 126–129 (1937).
[83] B. Rewald, *Biochem. Z.*, *211*, 199–201 (1929); *J. Soc. Chem. Ind.*, *56*, 77–78T (1937).
[84] Thus, for example, H. Thaler and W. Groseff, *Fette u. Seifen*, *50*, 472–475 (1943), found that of the 1.6–2.7% unsaponifiable matter in wheat germ oils, 70–85% consisted of sterols.

However, they are ordinarily of little concern to the oil technologist, inasmuch as they are chemically inert and do not contribute to any important property of the oil. Their recovery from oils is of some interest because they constitute starting materials for the synthesis of sex hormones and the artificial preparation of vitamin D. They may be separated from the other unsaponifiable constituents of fats by fractional crystallization, and may be concentrated from oils without saponification of the latter, by means of molecular distillation. Sterols occur in fats and oils in the free form, as esters of the fatty acids, and as glucosides. Alkali refining of oils removes a portion of the sterols, hence the soapstock resulting from this operation constitutes a rich source of sterols.[85] The sterol content of oils may also be appreciably reduced by high-temperature steam deodorization.[86,86a]

The characteristic sterol of animal fats is *cholesterol*, $C_{27}H_{46}O$; the sterols of vegetable oils apparently consist in most cases of a mixture of different members. The vegetable oil sterols are known collectively as *phytosterols*. Two phytosterols, *β-sitosterol*. $C_{29}H_{50}O$, and *stigmasterol*, $C_{29}H_{48}O$, have been definitely characterized.[87] The structure of the sterols is represented as follows:
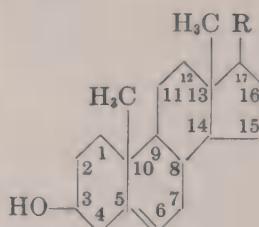
In the respective cases of the three sterols mentioned, the radical designated as R has the following forms:

$$-CH(CH_3)(CH_2)_3CH(CH_3)_2 \qquad -CH(CH_3)CH_2CH_2CHCH(CH_3)_2$$
$$C_2H_5$$

       Cholesterol   β-Sitosterol

$$-CH(CH_3)CH=CHCHCH(CH_3)_2$$
$$C_2H_5$$
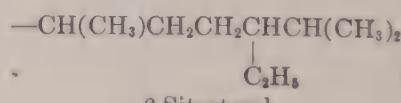
          Stigmasterol

γ-Sitosterol is considered a probable isomer of *β*-sitosterol. "*α*-Sitosterol,"

[85] See, for example, E. Holz, *Seifensieder Ztg.*, **56**, 140–141 (1928). Soapstock from the caustic washing stage of the Clayton continuous soda ash refining process is said to be particularly rich in sterols and other unsaponifiable constituents (see M. Mattikow, *J. Am. Oil Chem. Soc.*, **25**, 200–203 (1948)). For patents covering the commercial recovery of sterols from soapstock, see page 617.

[86] E. H. Melvin and J. E. Hawley, *Abstracts of Papers, 41st Annual Meeting American Oil Chemists' Society*, 1950.

[86a] R. H. Neal (to Best Foods, Inc.), U. S. Pat. 2,351,832 (1944).

[87] B. E. Bengtsson, *Z. physiol. Chem.*, **237**, 46–51 (1935).

once thought to be another isomer, has been shown[87-89] to be a mixture of at least three different compounds, which have been designated a_1-, a_2-, and a_3-. However, the structure of the a-sitosterols has never been definitely established.[88]

Campesterol differs from β-sitosterol in having a methyl group rather than an ethyl group substituted in the side chain.[90] It occurs in soybean oil. *Ergosterol*, which has been detected in small proportions in cottonseed oil[91] and palm oil,[92] is similar to stigmasterol, except that it has a methyl group in the side chain, and conjugated double bonds in the ring system, in the 5:6 and 7:8 positions.

Brassicasterol, like campesterol, a constituent of rapeseed oil, is similar to ergosterol except for the absence of the 7:8 double bond.

The mixed sterols of most fats and oils have not been subjected to exhaustive examination. Notable, however, is the very careful examination of cottonseed oil sterols carried out by Wallis and Chakravorty.[93] These workers found the mixed sterols to consist largely of β-sitosterol. A trace (0.9%) of *stigmastanol* was isolated (a compound of the same structure as stigmasterol, but completely saturated), but stigmasterol, γ-sitosterol, or a-sitosterols could not be found. On the other hand, in soybean oil a substantial proportion of the total sterols (up to 25%) consists of stigmasterol. It would thus appear that different vegetable oils have distinctive proportions of the different sterols, although the patterns of sterol content for the individual oils are largely unknown.

Of the products mentioned above, artificial vitamin D has apparently been made commercially only from cholesterol, whereas both cholesterol and soybean oil sterols have served as the starting materials for hormone manufacture.

The sterols provide a means of distinguishing between fats of animal and of vegetable origin, since the melting point of cholesterol acetate (114°C.) is substantially lower than that of the acetates of any of the phytosterols (126–137°C.).[94] The admixture of minor proportions of vegetable fats in animal fats can usually be detected, but the detection of animal fats in vegetable fats is less certain because of the variety of sterols occurring in the latter.[95]

[88] S. Bernstein and E. S. Wallis, *J. Org. Chem., 2*, 341–345 (1937); *J. Am. Chem. Soc., 61*, 1903–1904, 2308–2313 (1939). S. Bernstein, E. J. Wilson, Jr., and E. S. Wallis, *J. Org. Chem., 7*, 103–110 (1942).

[89] E. S. Wallis and E. Fernholz, *J. Am. Chem. Soc., 58*, 2446–2448 (1936).

[90] E. Fernholz and W. L. Ruigh, *J. Am. Chem. Soc., 63*, 1157–1159 (1941).

[91] A. Windaus and F. Bock, *Z. physiol. Chem., 250*, 258–261 (1937).

[92] R. F. Hunter, A. D. Scott, and J. R. Edisbury, *Biochem. J., 36*, 697–702 (1942). R. F. Hunter, A. D. Scott, and N. E. Williams, *ibid., 38*, 209–211 (1944).

[93] E. S. Wallis and P. N. Chakravorty, *J. Org. Chem., 2*, 335–340 (1937).

[94] The melting point of the mixed acetates of the sterols of vegetable oils is usually over 125°C., although there are some exceptions to this rule.

[95] For detailed information concerning the detection of animal-vegetable fat mixtures, see the monograph of G. S. Jamieson, *Vegetable Fats and Oils*, 2nd ed., Reinhold, New York, 1943.

The sterol contents of a number of crude fats and oils, according to Kaufmann[96] and Lange,[96a] are listed in Table 6.

TABLE 6

STEROL CONTENT OF FATS AND OILS (PER CENT)

Beef tallow	0.08–0.14	Olive oil	0.23–0.31
Butterfat	0.24–0.50	Palm oil	0.03
Castor oil	0.5	Palm kernel oil	0.06–0.12
Cocoa butter	0.17–0.20	Peanut oil	0.19–0.25
Coconut oil	0.06–0.08	Poppyseed oil	0.25
Cod liver oil	0.42–0.54	Rapeseed oil	0.35–0.50
Corn oil	0.58–1.0	Rice bran oil	0.75
Cottonseed oil	0.26–0.31	Sesame oil	0.43–0.55
Fish oil (Japanese)	0.3	Shea fat	0.09
Halibut liver oil	7.6	Soybean oil	0.15–0.38
Lard	0.11–0.12	Wheat germ oil	1.3–1.7
Linseed oil	0.37–0.42	Commercial shortenings and	
Mowrah fat	0.04	margarine oils (hydrogen-	
Mutton tallow	0.03–0.10	ated cottonseed and soy-	
		bean oil)	0.15–0.24

(b) Fatty Alcohols

Fatty alcohols, both in the free state and in combination with fatty acids as waxes, are found in quantity in many marine oils, but do not occur to any important extent in land animal or vegetable oils. However, some vegetable oils, including linseed, corn, and soybean oils contain sufficient quantities of wax (derived from the seed coat) to cause them to cloud when chilled to a low temperature. Corn oil wax was examined by Shriver, Nabenhauer, and Anderson,[97] who found it to consist of a mixture of the esters of myricyl alcohol with n-lignoceric and iso-behenic acids. However, Jamieson[98] reported that a sample of corn oil wax examined by him consisted principally of the esters of cetyl alcohol. Earle and Detwiler[99] found the wax of soybean oils to consist of a complex mixture of esters. The principal alcohols ranged from C_{32} to below C_{28}, while the acids had an average chain length of C_{22}. The wax amounted to no more than 0.002% of the oil.

3. COMPONENTS AFFECTING THE APPEARANCE OF OILS

The characteristic yellow-red color of most fats and oils is due to the

[96] H. P. Kaufmann, Fette u. Seifen, 48, 53–59 (1941).
[96a] R. L. Shriver, F. P. Nabenhauer, and R. J. Anderson, J. Am. Chem. Soc., 49.
[97] R. L. Shriver, F. P. Nabenhauer, and R. J. Anderson, J. Am. Chem. Soc., 49, 1290–1294 (1927).
[98] G. S. Jamieson, Vegetable Fats and Oils, 2nd ed., Reinhold, New York. 1943. p. 180.
[99] F. R. Earle and S. B. Detwiler, Jr., Oil & Soap, 18, 117–119 (1941).

presence of various carotenoid pigments. Structurally, the carotenoids consist of highly unsaturated hydrocarbon chains, or isoprene units, arranged in various cyclic and acyclic configurations. The structure of β-carotene, is representative:
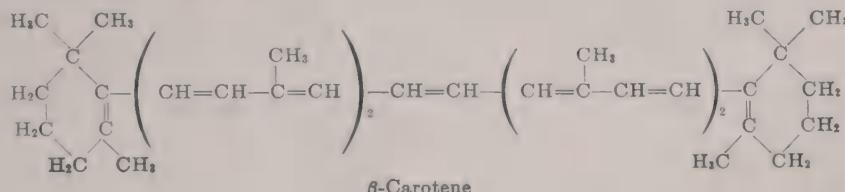
β-Carotene

Hydrogenation of an oil will reduce the unsaturation of its carotenoid pigments sufficiently to effect a significant reduction in color. These pigments are also to some degree unstable to heat, hence oils are bleached by high-temperature treatment, as in steam deodorization. Their chromogenic properties may be destroyed by oxidation, although ordinarily appreciable bleaching of an oil does not occur until oxidation has progressed to the point of producing rancidity or near rancidity. Limited oxidation ordinarily darkens vegetable oils. This darkening has been shown[100] to be due to the production of chroman-5,6-quinones (compounds related to the tocopherols) from a colorless precursor (γ-tocopherol), rather than to reactions involving carotenoids. True carotenoids apparently do not recolor upon oxidation, this being the observation, at any rate, with respect to those occurring in palm oil.[101] The carotenoids are readily adsorbed by Fuller's earth or activated carbon, hence the color of an oil pigmented solely by these compounds may be reduced to any desired value by sufficiently intensive treatment with adsorbents. Palm oil is much the highest of the various oils in carotenoid pigments, containing as much as 0.1% a- and β- carotene.

Cottonseed oil presents a somewhat unique picture among the industrially important fats and oils, in the great complexity of its pigment system. Most of the color of the crude oil is attributable to pigments of the gossypol type, and there is reason to believe that these pigments may also contribute substantially to the red-yellow color of the refined oil.[102]

Certain fats and oils, notably olive oil, soybean oil derived from green beans, and some inedible tallows, have a greenish color from the presence of chlorophyll or related compounds. Except in olive oil, a green color is generally undesirable. Green color presents a problem chiefly in the processing of soybean oil to produce edible products. Hydrogenated

[100] C. Golumbic, J. Am. Chem. Soc., 64, 2337–2340 (1942). C. E. Swift, G. E. Mann, and G. S. Fisher, Oil & Soap, 21, 317–320 (1944).
[101] P. Dubouloz and S. Lalement. Bull. mat. inst. colonial Marseille. 29, 35–38 (1945).
[102] For a comprehensive review of the involved chemistry of cottonseed pigments, see C. H. Boatner, Chapter VI, in Cottonseed and Cottonseed Products, A. E. Bailey, ed., Interscience, New York, 1948.

soybean oil frequently has a distinctly greenish cast, because the red and yellow pigments of this oil—which ordinarily mask green color—are very readily reduced by hydrogenation. Normal soybean oil is said[102a] to contain *ca.* 1500 µg. chlorophyll per liter.

A slight blue color sometimes observed in lard is not due to chlorophyll, but to some other pigment of unknown nature, which tends to be destroyed by oxidation. Margarine and other fat products containing moisture may rarely assume a pinkish color, from fat-soluble pigments produced by certain microorganisms.[103]

Certain brownish pigments, which do not appear in oils of good quality, but may be found in oils derived from damaged materials, appear to be decomposition products of proteins, carbohydrates, etc. Some of these are exceedingly difficult to remove by ordinary processing methods.[104]

4. Components Affecting the Stability of Oils

It has long been recognized that, because of their content of minute amounts of substances capable of powerfully inhibiting oxidation, natural fats and oils are much more resistant to oxidative deterioration than are pure triglycerides. In spite of notable contributions to the knowledge of oil and fat antioxidants in recent years, both the nature and the mode of action of these substances are still but imperfectly understood.[105]

(a) Tocopherols

One important class of antioxidants of almost universal distribution consists of the tocopherols, which are identical with vitamin E and were first isolated and characterized by workers in the field of nutrition. The tocopherols, discovered and named by Evans and co-workers,[106] were demonstrated by Olcott and Emerson[107] to be effective antioxidants, and to be the active substances in the "inhibitols" previously isolated from a variety of vegetable oils by Olcott and Mattill.[108] Three different tocopherols were identified by the earlier workers, and designated as *α*-, *β*-, and *γ*-. *β*- and *γ*-tocopherols differ from *α*-tocopherol in having one less methyl group substituted in the benzene ring. In *β*-tocopherol the methyl

[102a] W. C. Pritchett, W. G. Taylor, and D. M. Carroll, *J. Am. Oil Chem. Soc.*, *24*, 225–227 (1947).

[103] L. B. Jensen and D. P. Grettie, *Food Research*, *2*, 97–120 (1937).

[104] Badly field-damaged soybean oil is, in particular, very difficult to reduce to an acceptable color by alkali refining and adsorption bleaching.

[105] A review of natural vegetable oil antioxidants has been furnished by H. S. Olcott and H. A. Mattill, *Chem. Revs.*, *29*, 257–268 (1941). For reviews of the chemistry of the tocopherols, see L. I. Smith, *Chem. Revs.*, *27*, 287–329 (1940) and W. John. *Ergeb. Physiol. biol. Chem. exptl. Pharmakol.*, *42*, 1–52 (1939).

[106] H. M. Evans, O. H. Emerson, and G. A. Emerson, *J. Biol. Chem.*, *113*, 319–332 (1936). O. H. Emerson, G. A. Emerson, A. Mohammad, and H. M. Evans, *ibid.*, *122*, 99–107 (1937).

[107] H. S. Olcott and O. H. Emerson, *J. Am. Chem. Soc.*, *59*, 1008–1009 (1937).

[108] H. S. Olcott and H. A. Mattill, *J. Am. Chem. Soc.*, *58*, 1627–1630 (1936).
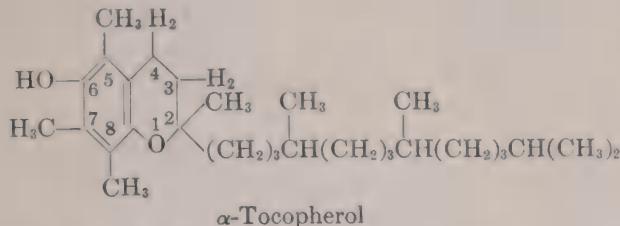
α-Tocopherol

groups are in the 5 and 8 positions, and in γ-tocopherol they are in the 7 and 8 positions. Recently, another, δ-tocopherol, has been isolated by Stern and co-workers.[109] This tocopherol is likewise an antioxidant, but it behaves differently from the others in the Emmerie-Engel test commonly used for tocopherol assay. It has been found in cottonseed, peanut, and wheat germ oils, and in soybean oil it is reported to comprise as much as 30% of the total tocopherols. Traces appear to occur in lard.[110] δ-Tocopherol is believed to have a single methyl group in the benzene ring, in the 8 position. γ-Tocopherol has been shown by Olcott and Emerson[107] to be a more effective antioxidant than β-tocopherol, which is in turn more effective than a-tocopherol. The antioxidant activity of δ-tocopherol, according to Stern et al.,[109] exceeds that of γ-tocopherol. The preceding data apply primarily to antioxidant action in fats subjected to heat to accelerate oxidation. It has been claimed that at ordinary atmospheric temperatures the three tocopherols are approximately equal in antioxidant activity.[111]

Like other antioxidants, the tocopherols are themselves readily oxidizable. Mild oxidation of a tocopherol opens the heterocyclic ring, to form tocoquinone, which is not an antioxidant. Golumbic[112] estimated that tocoquinones reached a maximum concentration of about 0.06% in the autoxidizing crude ethyl esters from a hydrogenated cottonseed oil. Under similar mild oxidizing conditions γ-tocopherol, but not a- or β-tocopherols, is partially converted to chroman-5,6-quinone.[112] This compound is of particular interest in oil and fat technology because of its dark red hue, which is sufficiently intense to cause a very noticeable intensification of the red-yellow color of partially oxidized edible vegetable oils. Chroman-5,6-quinone has feeble antioxygenic properties.

α-Tocoquinone
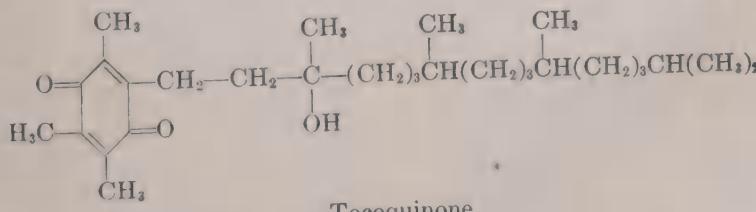
[109] M. H. Stern, C. D. Robeson, L. Weisler, and J. G. Baxter, J. Am. Chem. Soc., 69, 869–874 (1947).
[110] J. R. Chipault and W. O. Lundberg, Arch. Biochem., 12, 317–318 (1947).
[111] E. L. Hove and Z. Hove, J. Biol. Chem., 156, 623–632 (1944).
[112] C. Golumbic, Oil & Soap, 20, 105–107 (1943).

Chroman-5,6-quinone
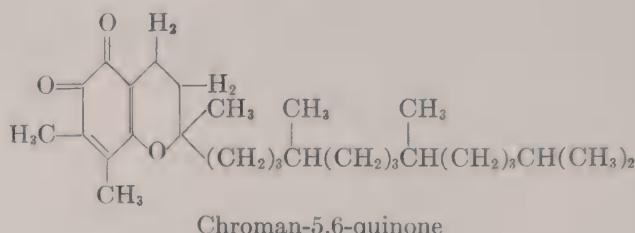
Analyses of different oils for tocopherols are given in Table 7. β-Tocopherol, which is not listed in the table, has been found only in wheat

TABLE 7

TOCOPHEROL CONTENT OF FATS AND OILS[a]

Oil	Alpha, %	Gamma, %	Delta, %	Total, %
Babassu, crude......	—	—	—	0.003
Beef tallow.........	—	---	—	0.001
Butterfat............	—	—	—	0.002–0.004
Castor..............	—	—	—	0.05
Cocoa butter........	—	—	---	0.003–0.013
Coconut............	0.0036	—	—	0.0083
Cod Liver Oil.......	—	—	—	0.026
Corn, refined........	0.009	0.081	—	0.090
Cottonseed, crude.....	0.076	0.034	—	0.110
Cottonseed, refined....	0.060–71	0.024–27	—	0.087–95
Cottonseed..........	0.041	0.036	0.009	0.086
Lard................	—	—	—	0.0005–29
Lard...............	0.0023	—	—	0.0027
Linseed oil,.........	—	—	—	0.11
Okraseed............	0.031	0.043	—	0.074
Oleo oil............	—	—	—	ca. 0.002
Olive..............	—	—	—	0.003–0.030
Palm...............	0.030	—	—	0.056
Peanut, crude........	0.018–30	0.018–22	—	0.036–52
Peanut, refined.......	0.024	0.024	—	0.048
Peanut.............	0.013	0.014	0.007	0.086
Pecan, refined........	0.020	0.022	—	0.042
Rice bran, crude......	0.075	0.026	---	0.101
Rice bran, refined.....	0.058	0.033	—	0.091
Safflower, crude.......	—	—	—	0.080
Sesame, refined.......	—	—	—	0.018
Soybean, refined......	0.020–21	0.074–78	—	0.094–99
Soybean............	0.020	0.098	0.050	0.168
Sunflowerseed oil.....	—	—	—	0.07
Wheat germ, crude....	—	—	—	0.18–0.45

[a] W. Lange, *J. Am. Oil Chem. Soc.*, *27*, 414–422 (1950).

germ oil. Tocopherol concentrates are prepared commercially by the molecular distillation of vegetable oils or of the sludges or distillates from

the steam deodorization of such oils, which constitute a rich source material.

The loss of tocopherols in commercial processing of edible vegetable oil products is relatively small. A maximum of about 6% of the total has been reported lost in bleaching or in continuous alkali refining, and no more than a few per cent in deodorizing, whereas hydrogenation occasions no loss whatsoever.[114]

(b) Other Antioxidants

Although the tocopherols may be considered the chief antioxidants of vegetable oils, there are undoubtedly others as yet unidentified. In this connection sesame and rice bran oils are of particular interest. These oils, particularly after hydrogenation, are significantly more stable than such oils as cottonseed, soybean, or peanut oils of equivalent unsaturation. The tocopherol content of these oils is not unusually high, and in any case it has been demonstrated[115] that extremely high stability is not imparted to an oil simply by a high tocopherol content, since the tocopherols exhibit their maximum effect at relatively low levels of concentration. Hence the high stability of sesame and rice bran oils is evidently due to the presence of antioxidants more potent that tocopherols.[116]

Gossypol, a complex phenolic substance occurring in crude, but not in refined, cottonseed oil has been shown by Royce[117] to have strong antioxygenic properties. The natural antioxidants appear to be generally high in molecular weight and nonvolatile, since they largely persist through the rather drastic treatment of high-temperature steam deodorization.

Phosphatides are not antioxidants when present alone in oils, but some phosphatides are capable of reinforcing the action of tocopherols or other antioxidants of the phenolic type. In commercial preparations of mixed phosphatides, Olcott and Mattill[118] have shown that antioxygenic activity is confined to the cephalin fraction. Phosphoric acid and other acids and acid substances similarly reinforce the action of phenolic anti-oxidants, and the antioxygenic activity of cephalin, in contrast to the lack of activity of lecithin, is attributed to the presence in the former of a

[113] C. E. Swift, G. E. Mann, and G. S. Fisher, *Oil & Soap*, *21*, 317–320 (1944).

[114] H. W. Rawlings, N. H. Kuhrt, and J. G. Baxter, *J. Am. Oil Chem. Soc.*, *25*, 24–26 (1948).

[115] See, for example, G. D. Oliver, W. S. Singleton, and A. E. Bailey, *Oil & Soap*, *21*, 188–193 (1944).

[116] Sesamol, a phenolic compound appearing in sesame oil in the form of a glucoside, sesamoline, has been reported by H. S. Olcott and H. A. Mattill, *Chem. Revs.*, *29*, 257–268 (1941), to have antioxygenic properties. See also P. Budowski, F. G. T. Menezes, and F. G. Dollear, *J. Am. Oil Chem. Soc.*, *27*, 377–380 (1950).

[117] H. D. Royce, *Oil & Soap*, *10*, 123–125 (1933). H. D. Royce and F. A. Lindsey, *Ind. Eng. Chem.*, *25*, 1047–1050 (1933).

[118] H. S. Olcott and H. A. Mattill, *Oil & Soap*, *13*, 98–100 (1936).

free hydroxyl group of phosphoric acid. The reinforcing or synergistic action of cephalin, like that of other acid inhibitors, is largely lost when the fat is incorporated into biscuits, crackers, or other baked goods.

5. COMPONENTS CONTRIBUTING TO FLAVOR AND ODOR

Relatively few of the compounds responsible for the flavor and odors of fats and oils have been identified. Certain ketones of high molecular weight were isolated from lauric acid-type oils by Haller and Lassieur[119] and Salway,[120] and from soybean oil by Schmalfuss and Treu.[121]

Most fats and oils contain appreciable amounts, e.g., 0.1–0.2%, of hydrocarbons, which appear with the sterols in the unsaponifiable fraction. *Squalene,* $C_{30}H_{50}$, a highly unsaturated hydrocarbon structurally related to the carotenes, is found in large quantities in some fish liver oils, and has been reported in fractional percentages (0.1–0.7%) in olive, rice bran, and wheat germ oils and in lesser amounts in many other oils.[122] *Gad-usene,* $C_{18}H_{32}$ another unsaturated hydrocarbon, has been isolated from fish liver, rice, and soybean oils.[123] Several other hydrocarbons, *pristane, zamene, cetorhinene,* etc., have been found in fish or fish liver oils. Marcelet[124] has reported the presence of a great variety of hydrocarbons, ranging in chain length from C_{13} to C_{36}, both saturated and unsaturated, in olive oil; and two unsaturated hydrocarbons, with chains of 15 and 19 carbon atoms, respectively, in peanut oil. Although classed here with the odoriferous components, it is uncertain whether hydrocarbons as a class contribute in a major way to the odor and flavor of oils. However, the hydrocarbon mixtures of Marcelet, recovered from deodorizer distillates, had a very strong and unpleasant odor.

From the fractional distillation and analysis of deodorizer distillates Jasperson and Jones[125] have estimated that the following amounts of terpenoid hydrocarbons occur in several oleic-linoleic acid oils: palm, 0.025%; peanut, 0.019%; cottonseed, 0.025%; sunflower, 0.0135%. The terpenoid fractions had a strong odor and a nauseating flavor. They confirmed the observation of previous workers that methyl nonyl ketone and other ketones contribute largely to the odor and flavor of coconut and palm kernel oils.

Altogether, the compounds contributing to flavor and odor are among the most difficult materials for study by the fat chemist. They occur

[119] A. Haller and A. Lassieur, *Compt. rend., 150,* 1013–1019 (1910); *151,* 697–699 (1911).
[120] A. H. Salway, *J. Chem. Soc., 111,* 407–410 (1917).
[121] H. Schmalfuss and A. Treu, *Biochem. Z., 189,* 49 (1927).
[122] K. Täufel, H. Heinisch, and W. Heimann, *Biochem. Z., 303,* 324–328 (1940). J. Fitelson, *J. Assoc. Official Agr. Chem., 26,* 506–511 (1943).
[123] J. Nakamiya, *Sci. Papers Inst. Phys. Chem. Research (Tokyo), 28,* 16–26 (1935).
[124] H. Marcelet, *J. pharm. chim., 24,* 213–225 (1936).
[125] H. Jasperson and R. Jones, *J. Soc. Chem. Ind., 66,* 13–17 (1947).

only in the merest traces and appear to be altered in some way by high-temperature steam distillation. The flavor and odor of an oil reconstituted from deodorized oil and deodorizer distillates is much different from that of the original oil.

The odoriferous components of vegetable oils are as a whole somewhat remarkable for their low volatility. Complete deodorization of most oils requires prolonged vacuum steam distillation at a highly elevated temperature, *e.g.*, 200–250°C.

Certain types of flavors and odors in fats do not arise simply from the presence of volatile and consequently removable components, but are intimately related to the fatty acid composition of the oils. In fish oils, in particular, it will be observed that the characteristic odor of the oils is not permanently removable by even the most drastic steam deodorization, but is recurrent upon slight oxidation of the oil. According to Davies and Gill,[126] fishiness is associated with the concurrent presence in the oil of nitrogenous compounds and highly unsaturated glycerides, and results from the chemical combination of the two during oxidation of the glycerides. On the other hand, Uyeno and Matsuda[126a] claim that fishy odor in marine oils is definitely associated with the unsaponifiable fraction rather than with unsaturated fatty acids.

Flavor development in deodorized fats as a result of limited oxidation is commonly termed "flavor reversion." It occurs in certain vegetable and land animal fats, as well as in fish oils, but is pronounced only in fats which contain fatty acids with more than two double bonds.

Peculiarly, a tendency to "revert" in flavor persists in soybean, linseed, and other linolenic acid oils after these oils have been hydrogenated to a degree which is apparently sufficient to eliminate all trienoic acids completely. In the hydrogenated fats it would appear, therefore, that linolenic acid is the precursor of a hydrogenated compound responsible for flavor reversion. It has been postulated by Lemon[64] that this hypothetical compound is 9:10, 15:16-octadecadienoic acid produced by hydrogenation of linolenic at the 12:13 double bond. Lemon's hypothesis is supported by the work of Taylor and co-workers[127]; on the other hand, some workers, notably Mattil,[128] maintain on the basis of convincing experimental evidence that flavor reversion is associated with the unsaponifiable fraction and that the glycerides are not involved. For further discussion of the controversial question of flavor reversion, see Chapter II.

[126] W. L. Davies and E. Gill, *J. Soc. Chem. Ind.*, 55, 141–146T (1936).
[126a] S. Uyeno and S. Matsuda, *J. Soc. Chem. Ind. Japan*, *63*, 1093–1094 (1942).
[127] W. G. Taylor, *J. Am. Oil Chem. Soc.*, *26*, 413–418 (1949). S. W. Thompson, W. G. Taylor, and A. R. Gudheim, *Proc. 2nd Conference on Flavor Stability in Soybean Oil and Soybean Oil Products*, Natl. Soybean Processors Assoc., Chicago, 1946.
[128] K. F. Mattil, *J. Am. Oil Chem. Soc.*, *24*, 243–246 (1947). *Proc. 2nd Conference on Flavor Stability in Soybean Oil and Soybean Oil Products*, Natl. Soybean Processors Assoc., Chicago, 1946.

6. COMPONENTS OF NUTRITIONAL SIGNIFICANCE

Fats and oils are important sources of the fat-soluble vitamins, A, D, and E.[129]
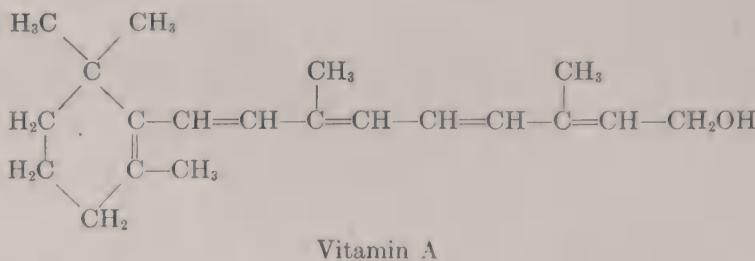
Vitamin A

Vitamin A may be considered to be derived from β-carotene (see page 29) by fissure of a molecule of the latter in the middle of the hydrocarbon chain, and the addition of one molecule of water to each fragment. Such conversion of β-carotene to vitamin A does in fact occur in the body of man and other animals; hence β-carotene is designated as provitamin A. The proportion of the provitamin actually converted to the vitamin is variable, but appears to be not greater than 50–60%. Certain other carotenoid pigments, for example, a-carotene and γ-carotene, are also provitamins but many are not; hence the depth of color in a fat is not a certain indication of its provitamin content, although in some fats, including butter, there is a rough correlation between the two.

Somewhat recently a "neo-vitamin A" has been reported in fish liver oils by Robeson and Baxter.[130] This compound, which has the same biological potency as normal vitamin A, contributes about 30% of the entire vitamin A content of certain oils. It is believed to be a geometrical isomer of vitamin A, differing in *cis-trans* configuration at the double bond nearest the hydroxyl group.

Vitamin D has had ascribed to it the following formula:

Natural vitamin D
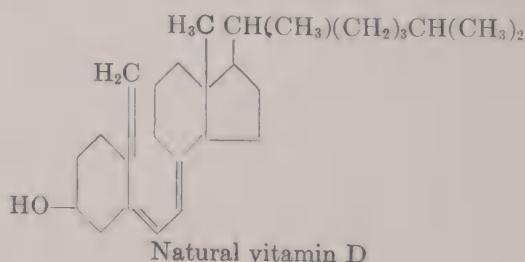
It is therefore related to the sterols (see page 26), its condensed ring system differing from that of the sterols in having the second benzene ring

[129] For late information on the fat-soluble vitamins, reference should be made the reviews published each year in *Annual Review of Biochemistry*.
[130] C. D. Robeson and J. G. Baxter, *Nature, 155,* 300 (1945); *J. Am. Chem. Soc.,* 136–141 (1947).

opened. A second form of vitamin D, called calciferol, can be prepared by the irradiation of ergosterol, or by the irradiation of cholesterol after suitable chemical treatment. This form has the same ring structure as that depicted above, but has a slightly different side chain. It is probable that there are in addition other forms of this vitamin.

Butter contains from 0.0003–0.0015% of vitamin A, in addition to an approximately equal amount of β-carotene[131] (see page 130). Oleo oil contains an appreciable amount of carotenes, and palm oil has a very high content of carotenes (about one-half a and one-half β[131a]) and a vitamin A potency by biological assay which may be as high as 400 U.S.P. units per gram.[131b] Most other vegetable oils appear to contain no important amount of either vitamin A or its provitamins, their yellow-red color apparently being derived from carotenoid pigments other than the precursors of vitamin A.

Butter also contains from 0.1 to 1.0 International Unit of vitamin D per gram[132]; the content of this vitamin, like that of vitamin A, being highest in the summer and lowest in the winter. Land animals fats and vegetable oils contain no appreciable amounts of vitamin D.

The body oils of most fishes and marine animals contain considerable amounts of vitamins A and D, for example about 500 and 100 U.S.P. units per gram, respectively, in the case of sardine, herring, and menhaden oils. Certain fish liver oils are extremely rich in these vitamins. Halibut and soup fin shark liver oils have been reported to contain 100,000 to 300,000 U.S.P. units of vitamin A per gram,[133] and vitamin D contents as high as 200,000 U.S.P. units per gram have been reported in tuna liver oils.

However, fish liver oils of very high vitamin A potency are not generally available in quantity, and the vitamin A concentrates of commerce are principally obtained from oils of low to medium vitamin A content, such

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[131] The biological activity depends upon the content of carotene or other provitamins, as well as the content of vitamin A or its esters. Unfortunately, both the International unit (I.U.) and the U.S.P. unit are based upon biological standards, and there is no clearcut correlation between the two, or between either and pure vitamin A (or vitamin A esters). See H. A. Ellenberger, N. B. Guerrant, and M. E. Chilcote, *J. Nutrition, 37,* 185–201 (1949). By definition, one I.U. is equivalent in biological activity to 0.6 μg. of beta carotene, whereas the U.S.P. unit is referred to that of a standard sample of cod liver oil. According to the best evidence, 1 g. of pure vitamin A (alcohol) is equivalent to about 3,400.000 I.U. or 4,300,000 U.S.P. units based on the old standard (U.S.P. Reference Cod Liver Oil No. 3) used prior to 1949. On the basis of the present standard, the I.U. and the U.S.P. unit are more nearly comparable (see Ellenberger *et al.*, above). It is probable that the present biological standards for vitamin A assay will eventually be replaced by a single more satisfactory chemical standard based on a pure vitamin A ester. See N. D. Embree *et al., Oil & Soap, 23,* 275–276 (1946); N. B. Guerrant, M. E. Chilcote, H. A. Ellenberger, and R. A. Dutcher, *Anal. Chem., 20,* 465–469 (1948).
[131a] R. F. Hunter and A. D. Scott, *Biochem. J., 38,* 211–213 (1944).
[131b] C. F. Poe and H. A. Fehlmann, *Food Research, 9,* 500–504 (1944).
[132] 1 I.U. is equivalent in biological activity to 0.025 μg. calciferol.
[133] See, for example, S. Springer and P. M. French, *Ind. Eng. Chem., 36,* 190–191 (1944). The vitamin A ester content of these high-potency oils amounts to several per cent.

as grayfish liver oils. These oils generally contain 10,000 to 15,000 U.S.P.
units of vitamin A per gram. Because of the cheapness of synthetic vita-
min D, fish liver oils are no longer important as sources of this vitamin.
In fish liver oils vitamin A exists almost entirely (96–100%) in the form
of fatty acid esters.[134]

The subject of vitamin E in oils has been covered in the previous dis-
cussion of tocopherols (page 30), with which this vitamin is identical.

7. MINERAL CONTENT

Even well-refined commercial fats will contain traces of phosphorus
from the presence of residual phosphatides (page 613) and traces (e.g.,
5–20 p.p.m.) of sodium soaps left from alkali refining.

The analysis of fats and oils for their content of heavy metals is difficult,
and relatively little data are as yet available. O'Connor and co-workers[135]
have found various crude vegetable oils to contain as much as 0.1–0.3
p.p.m. of copper, 0.1–0.7 p.p.m. of manganese, and 1–5 p.p.m. of iron.
Crude African peanut oil is said to be characteristically high in copper
content. It has been generally assumed that heavy metals are present in
commercial oils only through contact of the oil with metal processing
equipment, but this is probably not the case. There appears to be no rea-
son why metals in oils, as in other plant products, might not be derived
from the soils in which the plants are grown. Fats often contain appreci-
able amounts of nickel after hydrogenation, e.g., 0.1–0.2 p.p.m.

Ordinary alkali refining and adsorption bleaching, and in some cases,
bleaching alone, appear to remove heavy metals from oils quite effectively.
However, Melvin and Hawley[86] have found 0.1–2.5 p.p.m. of iron and
0.01–.02 p.p.m. of copper in a group of samples of commercial salad oils.

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[134] See G. Reed, E. C. Wise, and R. J. L. Frundt, *Ind. Eng. Chem., Anal. Ed., 16,*
509–510 (1944). Also H. M. Kascher and J. G. Baxter, *ibid., 17,* 499–503 (1945).
[135] R. T. O'Connor, D. C. Heinzelman, and M. E. Jefferson, *J. Am. Oil Chem. Soc.,*
25, 408–414 (1948).

REACTIONS OF FATS AND FATTY ACIDS

Some of the chemical reactions of fats and fatty acids are important because they are employed in the manufacture of fatty products. These will be discussed at length in the individual chapters devoted to specific unit processes. The present chapter will be concerned principally with reactions not given detailed consideration elsewhere, including those which form the basis of common analytical methods. However, for the sake of completeness, all of the more important reactions will be mentioned briefly.

Unlike most edible materials, fats and oils suffer relatively little spoilage or deterioration from bacterial action. Most of the damage incurred by fats in storage is the result of atmospheric oxidation. For this reason, particular attention will be given to the reaction occurring between fats and the oxygen in the air.

A. Hydrolysis, Esterification, and Related Reactions

1. HYDROLYSIS

Under the proper conditions, the triglycerides of fats and oils may be hydrolyzed, to yield free fatty acids and glycerol:

$$C_3H_5(OOC.R)_3 + 3\ HOH = C_3H_5(OH)_3 + 3\ HOOC.R$$

The reaction is reversible; if reactants and reaction products are not removed from the sphere of reaction, an equilibrium depending upon the concentrations of the former will eventually be reached. In practical fat splitting, a high degree of hydrolysis is insured by the provision of a large excess of water, and usually by repeatedly withdrawing the glycerol-rich aqueous phase and replacing it with fresh water. Hydrolysis is catalyzed by acids, compounds which form fatty acid soaps, and other substances, including lipolytic enzymes. The latter are distinctive in permitting rapid hydrolysis to take place at ordinary atmospheric temperatures. Commercial fat splitting is discussed at greater length on pages 796–806.

2. ESTERIFICATION

If the desired reaction is the reverse of that indicated above, it may be made substantially complete by continuously removing water from the reaction zone. By causing hydrolysis to take place, and then substituting another alcohol for glycerol in the reverse, or esterification, reaction fatty acid esters of any mono- or polyhydric alcohol may readily be formed.

If esterification is carried out with the polyhydric alcohol in excess of the fatty acids, partial esters, *e.g.*, mono- and diglycerides, are formed. Esterification is catalyzed by a number of materials, including many of those effective in promoting hydrolysis. For further discussion of the esterification reaction see Chapter XIX.

3. INTERESTERIFICATION

Esters of the lower alcohols, *e.g.*, methyl and ethyl alcohol, may also be prepared by reacting the alcohol directly with the fat to displace glycerol:

$$C_3H_5(OOC.R)_3 + 3\ CH_3OH = 3\ CH_3.OOC.R + C_3H_5(OH)_3$$
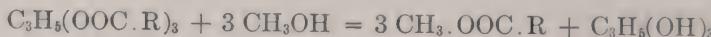
Low molecular weight acids of the fatty acid series can be made to displace high molecular weight fatty acids from glycerides by an analogous reaction. On the other hand, if the reaction is conducted at a high temperature and the relatively volatile lower alcohol is continuously vaporized and removed from the reaction zone, the reaction can be made to go in the reverse direction, with the formation of glycerides from esters of the lower alcohol.

Reaction of triglycerides with glycerol and a suitable catalyst will cause migration of fatty acid radicals, to form some proportion of mono- and diglycerides. If only a very small proportion of glycerol is reacted with the fat, migration and interchange of the fatty acid radicals will eventually lead to the production of triglycerides of new composition and structure without formation of any large proportion of partial esters. Similar rearrangement of glyceride structure can be accomplished without glycerol being present in excess with the assistance of certain catalysts. Most of the above interesterification reactions of glycerides have their counterparts in the reactions of fatty acid esters of polyhydric alcohols other than glycerol. All are treated at length in Chapter XIX.

4. SAPONIFICATION WITH ALKALIES

If the fat is split, not with the aid of water, but with an alkali, to yield glycerol and a salt or soap of the alkali metal, the reaction is termed saponification:

TABLE 8

MOLECULAR WEIGHTS AND SAPONIFICATION VALUES OF SATURATED FATTY ACIDS AND THEIR TRIGLYCERIDES

Common name	Systematic name	Number of C atoms	Molecular weight of the acid	Molecular weight of its triglyceride	Neutralization value of the acid	Saponification value of the triglyceride
Butyric	Butanoic	4	88.10	302.4	636.8	556.6
Caproic	Hexanoic	6	116.16	386.5	483.0	435.5
Caprylic	Octanoic	8	144.21	470.7	389.0	357.6
Capric	Decanoic	10	172.26	554.8	325.7	303.4
Lauric	Dodecanoic	12	200.31	639.0	280.1	263.4
Myristic	Tetradecanoic	14	228.36	723.1	245.7	232.8
Palmitic	Hexadecanoic	16	256.42	807.3	218.8	208.5
Stearic	Octadecanoic	18	284.47	891.5	197.2	188.8
Arachidic	Eicosanoic	20	312.52	975.6	179.5	172.5
Behenic	Docosanoic	22	340.57	1059.8	164.7	158.8
Lignoceric	Tetracosanoic	24	368.62	1143.9	152.2	147.1
Isovaleric	—	5	102.13	344.4	549.3	488.7

TABLE 9

MOLECULAR WEIGHTS AND SAPONIFICATION VALUES OF UNSATURATED FATTY ACIDS AND THEIR TRIGLYCERIDES

Fatty acid	Number of C atoms	Number of double bonds	Molecular weight of the acid	Molecular weight of its triglyceride	Neutralization value of the acid	Saponification value of the triglyceride
Decenoic	10	1	170.24	548.8	329.6	306.7
Dodecenoic (lauroleic)	12	1	198.29	632.9	282.9	265.9
Tetradecenoic (myristoleic)	14	1	226.34	717.1	247.9	234.7
Hexadecenoic (palmitoleic)	16	1	254.39	801.2	220.5	210.1
Octadecenoic (oleic, etc.)	18	1	282.44	885.4	198.6	190.1
Eicosenoic (gadoleic)	20	1	310.50	969.5	180.7	173.6
Docosenoic (erucic, etc.)	22	1	338.55	1053.7	165.7	159.7
Tetacosenoic (selacholeic)	24	1	366.60	1137.9	153.0	147.9
Octadecadienoic (linoleic)	18	2	280.43	879.3	200.0	191.4
Hexadecatrienoic	16	3	250.36	789.2	224.1	213.3
Octadecatrienoic (linolenic, etc.)	18	3	278.41	873.3	201.5	192.7
Octadecatetraenoic	18	4	276.40	867.3	203.0	194.1
Eicosatetraenoic (arachidonic, etc.)	20	4	304.45	951.4	184.3	176.9
Eicosapentaenoic	20	5	302.43	945.3	185.5	178.1
Docosapentaenoic	22	5	330.49	1029.5	169.8	163.5
Docosahexaenoic	22	6	328.47	1023.5	170.8	164.4
Tetracosapentaenoic	24	5	358.54	1113.7	156.5	151.1
Tetracosahexaenoic	24	6	356.52	1107.6	157.4	152.0
Hexacosapentanoic	26	5	386.59	1197.8	145.1	140.5
Hexacosahexaenoic	26	6	384.57	1191.8	145.9	141.2
Ricinoleic	18	1	298.44	933.4	188.0	180.3
Licanic	18	3	292.39	915.2	191.9	183.9

$$C_3H_5(OOC.R)_3 + 3 NaOH = C_3H_5(OH)_3 + 3 NaOOC.R$$

This reaction, which forms the foundation of the soapmaking industry, is discussed in Chapter XX.

Soaps may of course also be made by reacting the free acids with an alkali, water being set free in the reaction.

The reaction between an alkali and fat or fatty acids is the basis of two important analytical determinations. The *acid value* is a measure of the hydrolysis that has occurred in a fat, and is defined as the number of milligrams of potassium hydroxide required to neutralize the free fatty acids in one gram of fat. The acidity of fats is also often expressed directly in terms of per cent *free fatty acids* (usually abbreviated F.F.A.), the assumption usually being made in the calculation that the acids have a molecular weight equal to that of oleic acid. The relation between acid value and per cent free fatty acids calculated as oleic is as follows: 1 unit of acid value = 0.503% free fatty acids.

The saponification value and certain related values are measures of the *average molecular weight* in fatty materials. The *saponification value* is defined as the number of milligrams of potassium hydroxide required to saponify one gram of fat. The *neutralization value* is the number of milligrams of potassium hydroxide required to neutralize one gram of fatty acids. The *saponification equivalent* (sometimes referred to as the *neutralization equivalent* when applied to fatty acids) is the number of grams of material saponified by one mole, or 56.104 grams of potassium hydroxide. It is thus numerically equal to the mean molecular weight of the acids, if the material consists of *pure fatty* acids, or equal to one-third the mean molecular weight of the glycerides, if it is assumed that the material consists entirely of neutral oil, free of unsaponifiable matter or other impurities. The *ester value* is the number of milligrams of potassium hydroxide required to saponify the neutral oil in a one-gram sample, exclusive of that required to neutralize any free acids, and hence is equal to the saponification value minus the acid value. The following relation holds between the saponification value and the saponification equivalent: (saponification value) (saponification equivalent) = 56,104. The relationship between neutralization value and neutralization equivalent is, of course, similar.

The molecular weights and calculated saponification-neutralization values of the more common fatty acids and their triglycerides are given in Tables 8 and 9.

B. Other Reactions Involving the Carboxyl Group

1. FORMATION OF METAL SOAPS

As mentioned above, the fatty acids react readily with sodium or potassium oxides, hydroxides, carbonates, etc., to produce soaps:

$$NaOH + R.COOH \longrightarrow R.COONa + H_2O$$
$$K_2CO_3 + 2 R.COOH \longrightarrow 2 R.COOK + H_2O + CO_2$$
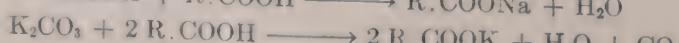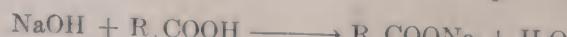
Corresponding compounds of the alkali metals react similarly, although somewhat less readily:

$$Ca(OH)_2 + 2 R.COOH \longrightarrow (R.COO)_2Ca + 2 H_2O$$

Reaction of the fatty acids with corresponding compounds of such metals as zinc, lead, manganese, cobalt, or tin is still more difficult, but may be accomplished slowly at elevated temperatures. It is usually more feasible to prepare soaps of the heavy metals by double decomposition of a sodium or potassium soap and a salt of the metal. The following reaction is typical of the latter method:

$$2 NaOOC.R + Pb(OOC.CH_3)_2 = Pb(OOC.R)_2 + 2 NaOOC.CH_3$$

Commercially, the above reactions are carried out on a large scale, particularly in the manufacture of lubricating greases (see pages 490–494) and metallic dryers for paints and other protective coatings (pages 446–448).

2. Hydrogenation in the Carboxyl Group

Reacted under the proper conditions with a suitable catalyst, fatty acids can add hydrogen in the carboxyl group to form fatty alcohols:

$$R.COOH + 2 H_2 \longrightarrow R.CH_2.OH + H_2O$$

By a comparable reaction fatty alcohols may be prepared by the hydrogenation of glycerides or other esters:

$$R.COOR' + 2 H_2 \longrightarrow R.CH_2OH + R'OH$$

They may also be prepared by the sodium reduction of fatty acids in alcohol:

$$R.COOH + 4 Na + 4 C_2H_5OH \longrightarrow R.CH_2.OH + 4 NaOC_2H_5 + H_2O$$

Both of the above reactions are used in the commercial preparation of fatty alcohols (see Chapter XVII).

3. Formation of Nitrogen Derivatives

In the presence of ammonium chloride and certain other catalysts fatty acids react with liquid ammonia to form amides:[1]

$$R.COOH + NH_3 \longrightarrow R.CONH_2 + H_2O$$

Amides undergo dehydration at an elevated temperature to form the corresponding nitriles:

$$R.CONH_2 \longrightarrow R.CN + H_2O$$

[1] R. Oda and S. Wada, *J. Soc. Chem. Ind. Japan*, *37*, 295–296 (1934). V. F. Balaty, L. L. Fellinger, and L. F. Audrieth, *Ind. Eng Chem.*, *31*, 280–282 (1939).

Upon catalytic hydrogenation, nitriles are converted into the corresponding primary or secondary amines:

$$R.CN + 2 H_2 \longrightarrow R.CH_2.NH_2$$
$$2 R.CN + 4 H_2 \longrightarrow (R.CH_2)_2NH + NH_3$$
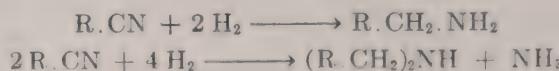
The preceding reactions are all utilized in the preparation of nitrogen-containing fatty acid derivatives; the commercial production of these has been described by Kenyon et al.[1a] and by Potts and McBride.[1b]

4. FORMATION OF ACID CHLORIDES

Acid chlorides may be prepared[2] by reacting fatty acids with various reagents, of which phosphorus trichloride, PCl_3, phosphorus pentachloride, PCl_5, thionyl chloride, $SOCl_2$, and oxalyl chloride, $(COCl)_2$, are the ones most commonly employed:

$$3 R.COOH + PCl_3 \longrightarrow 3 R.COCl + H_3PO_3$$
$$R.COOH + PCl_5 \longrightarrow R.COCl + POCl_3 + HCl$$
$$R.COOH + SOCl_2 \longrightarrow R.COCl + SO_2 + HCl$$
$$R.COOH + (COCl)_2 \longrightarrow R.COCl + HCl + CO_2 + CO$$
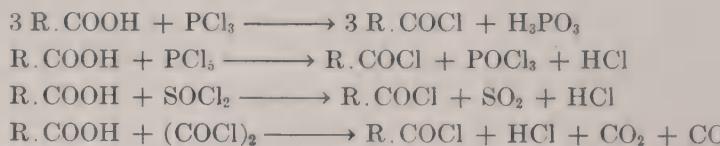
Although the acid chlorides are not prepared technically in large quantities, they are of considerable importance in oil and fat chemistry, inasmuch as they serve as intermediates for the production of synthetic glycerides and waxes, and a wide variety of other fatty acid derivatives. The chlorine atom is highly labile, and readily replaced by a number of other groups. The following reactions are typical:

$$R.COCl + HO.R \longrightarrow R.COO.R + HCl$$
$$R.COCl + NH_2.R \longrightarrow R.CO.NH_2 + HCl$$
$$R.COCl + NaO.CO.R \longrightarrow R.COO.CO.R + NaCl$$
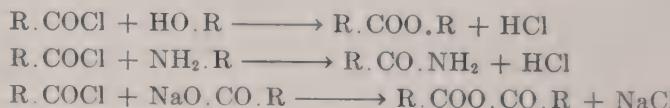
C. Reactions in the Fatty Acid Chain

Most of the reactions which occur in the fatty acid chains involve addition at the double bonds of unsaturated fatty acids, although in a few cases substitution may occur in saturated acids, with the replacement of hydrogen atoms by other atoms or groups. In general, reactions of this type occur with more or less equal facility in the free acids, the glycerides, or other esters or salts of the acids.

1. HYDROGENATION

In the presence of a suitable catalyst, gaseous hydrogen is readily added

[1a] R. L. Kenyon, D. V. Stingley, and H. P. Young, Ind. Eng. Chem., 43, 203–213 (1950).
[1b] R. H. Potts and G. W. McBride. Chem. Eng., 57, No. 2. 124–127 (1950).
[2] See S. T. Bauer, Oil & Soap, 23, 1–5 (1946).

at the double bonds of unsaturated fatty acids, to transform these acids to the corresponding saturated acids, or to reduce their degree of unsaturation. Catalytic hydrogenation is carried out commercially on a very wide scale, as described in Chapter XVII.

Theoretically, the hydrogen absorption is the best index of the degree of unsaturation in a fat, inasmuch as hydrogen is added quantitatively at the double bonds, without the possibility, as in halogen addition, etc., of addition being incomplete, or of substitution or other side reactions occurring. However, the *hydrogen number* of fats is seldom determined as an analytical characteristic, owing to the mechanical difficulties involved in carrying out accurate measurements of hydrogen absorption.

2. Dehydrogenation

Theoretically, it would appear that *dehydrogenation* might be accomplished under suitable conditions and that this would afford a ready means of increasing the unsaturation of oils. Such, however, is apparently not the case. Levey[3] and also Raymond and Moretti[4] have claimed extensive dehydrogenation of glycerides or other esters with the assistance of hydrogenation catalysts. However, Suzuki and Kurita[5] and Forbes and Neville[6] were unable to produce a significant amount of dehydrogenation, using a wide variety of catalysts. Margaillan and Angeli[7] have reported the conversion of methyl stearate to oleic acid in the vapor phase, vapors of the ester being mixed with ethylene and passed over a nickel catalyst at 190–220°C.

3. Halogenation

Chlorine, bromine, and iodine, and also iodine monochloride and iodine monobromide, may be added at the double bonds of unsaturated acids, as in the following example:
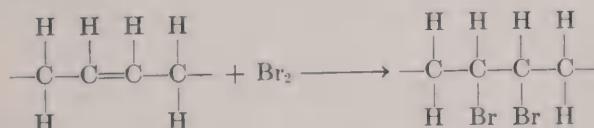
Addition takes place readily, but is quantitative or nearly quantitative only under special conditions, due to the tendency of the halogen to add incompletely or, in other cases, to displace hydrogen atoms.

The quantitative addition of iodine monobromide or iodine monochloride forms the basis of the important characteristic known as the *iodine*

[3] H. A. Levey, U. S. Pat. 1,374,589 (1921).
[4] E. Raymond and J. Moretti, *Compt. rend.*, 222, 893–895 (1938).
[5] T. Suzuki and R. Kurita, *Sci. Papers Inst. Phys. Chem. Research Tokyo*, Suppl. Bind., 9, 5–6 (1928).
[6] W. C. Forbes and H. A. Neville, *Ind. Eng. Chem.*, 32, 555–558 (1940).
[7] L. Margaillan and X. Angeli, *Compt. rend.*, 206, 1662–1663 (1938).

value, which is defined as the number of grams of iodine absorbed under standard conditions by 100 grams of fat. The iodine value represents the true unsaturation of fats or fatty acids only when the double bonds in the latter are unconjugated; halogen absorption is not quantitative in the case of conjugated fatty acids. The calculated iodine values of different unsaturated fatty acids and their triglycerides are listed in Table 10.

TABLE 10

IODINE VALUES OF UNSATURATED FATTY ACIDS AND THEIR TRIGLYCERIDES

Fatty acid	Number of C atoms	Number of double bonds	Iodine value of acid	Iodine value of triglyceride
Decenoic............................	10	1	149.1	138.77
Dodecenoic (lauroleic)..............	12	1	128.0	120.32
Tetradecenoic (myristoleic)..........	14	1	112.1	106.20
Hexadecenoic (palmitoleic)..........	16	1	99.78	95.04
Octadecenoic (oleic, etc.)............	18	1	89.87	86.01
Eicosenoic (gadoleic, etc.)...........	20	1	81.75	78.54
Docosenoic (erucic, etc.)............	22	1	74.98	72.27
Tetracosenoic (selacholeic, etc.)......	24	1	69.24	66.93
Octadecadienoic (linoleic, etc.).......	18	2	181.04	173.21
Hexadecatrienoic...................	16	3	304.17	289.48
Octadecatrienoic (linolenic, etc.).....	18	3	273.52	261.61
Octadecatetraenoic.................	18	4	367.35	351.21
Eicosatetraenoic (arachidonic, etc.)...	20	4	333.51	320.17
Eicosapentaenoic...................	20	5	419.67	402.79
Docosapentaenoic..................	22	5	384.04	369.85
Docosahexaenoic...................	22	6	463.68	446.42
Tetracosapentaenoic................	24	5	353.99	341.89
Tetracosahexaenoic.................	24	6	427.20	412.52
Hexacosapentaenoic................	26	5	328.31	317.88
Hexacosahexaenoic.................	26	6	396.04	383.38
Ricinoleic.........................	18	1	85.06	81.58

Since the bromine addition compounds of unsaturated fatty acids tend to become less soluble in cold ether and petroleum ether as the number of double bonds increases, mixed fatty acids are often brominated for the purpose of estimating or detecting the presence of highly unsaturated acids. The *hexabromide number* is the number of grams of insoluble bromides obtained from 100 grams of fatty acids under certain standard conditions. Once believed to indicate quantitatively the percentage of linolenic acid in the sample, it is now known to be influenced by the contents of other fatty acids.

Halogenation may also occur by substitution, with free or combined halogens replacing one or more hydrogen atoms in the hydrocarbon chain. Although substitution occurs most readily at the carbon atom next to the

carboxyl group, it is in most cases impossible to predict either the extent of substitution or the positions at which substitution will occur. Halogenation by substitution does not occur readily except under special conditions, such as prolonged exposure of the fat to an excess of halogen in certain solvents, or exposure to halogens in the presence of a catalyst, such as phosphorus.[8]

4. ADDITION OF THIOCYANOGEN

The reaction of unsaturated fatty acids and their esters with thiocyanogen (SCN) is important because it forms the basis of a common analytical method which provides more information concerning the composition of mixtures than do iodine values alone. Thiocyanogen was formerly believed to add quantitatively at one of the two double bonds of a nonconjugated diunsaturated acid, and at two of the three double bonds of a triunsaturated acid. It is now known that the extent of addition is variable according to the conditions of reaction (see page 126), but that it can be made reproducible by proper standardization of the latter. The official method of the American Oil Chemists' Society[8a] specifies a reaction time of 24 hours with 0.2 N lead thiocyanate solution. Under these conditions the empirical *thiocyanogen value* of oleic acid is 89.3, that of linoleic acid is 96.7, and that of linolenic acid is 167.1. Corresponding values for these acids combined as glycerides are 85.5, 92.5, and 159.8, respectively.

The thiocyanogen value is analogous to the iodine value, being calculated on the same basis, in terms of iodine.

5. ADDITION OF MALEIC ANHYDRIDE

The Diels-Alder reaction (page 414), in which maleic anhydride reacts with conjugated fatty acids, is the basis of the *diene value*, which like the thiocyanogen value is calculated in terms of equivalents of iodine. The theoretical diene value of elaeostearic acid combined in the form of glycerides is 87.2. However, it has been shown[9] that the actual diene value of conjugated acids is somewhat variable according to the conditions under which reaction is carried out.

At temperatures of about 200°C. and above, nonconjugated acids will also add maleic anhydride. According to Bickford and coworkers,[10] the amount combined ranges from nearly one mol per mol of acid for

[8] For a recent investigation of the chlorination of saturated fatty esters, see H. H. Guest and C. M. Goddard, Jr., *J. Am. Chem. Soc.*, *66*, 2074–2075 (1945).
[8a] American Oil Chemists' Society, *Official and Tentative Methods*, 2nd ed., V. C. Mehlenbacher, editor, Chicago, 1946. Method Cd 2–38.
[9] R. S. McKinney, N. J. Halbrook, and W. G. Rose, *Oil & Soap*, *19*, 141–143 (1942).
[10] W. G. Bickford, P. Krauczunas, and D. H. Wheeler, *Oil & Soap*, *19*, 23–27 (1942).

oleates, to 2.5 mols for linolenates. Since the unsaturation of polyethenoid acids and esters does not decrease in proportion to the amount added, it is apparent that in these, addition is not altogether by the Diels-Alder reaction following a shift of the double bonds to conjugated positions, but partially, as in the case of oleates, by an entirely different mechanism in which a double bond is not involved (see page 440). Drying oils are commercially "maleinized" to increase their reactivity.

6. SULFATION. SULFONATION

Unsaturated acids readily react with strong sulfuric acid with the introduction of either the sulfate group—OSO_2OH, or the sulfonate group,—SO_2OH at the double bond (see page 391). This reaction, followed by neutralization of the resulting sulfuric ester with sodium carbonate, is carried out commercially to an extensive degree, in the preparation of so-called sulfonated oils for the textile industry, etc.

7. CHEMICAL OXIDATION. HYDROXYLATION

Unsaturated fatty acids and their esters are readily oxidized by the usual chemical oxidizing agents, including nitric acid, chromic acid, ozone, potassium permanganate, and hydrogen peroxides and the various peracids, such as perbenzoic, persulfuric, performic, and peracetic acids. Saturated acids and their esters can also be oxidized by chemical oxidizing agents, but much less readily. Such reactions are potentially important from an industrial standpoint, and they form the basis of certain useful analytical methods.

Under mild oxidizing conditions, and particularly in an aqueous medium, unsaturated acids and esters tend to form polyhydroxy acids; the following reaction of oleic acid is typical:

$$CH_3(CH_2)_7CH=CH(CH_2)_7COOH \; + \; O \; + \; H_2O \longrightarrow$$

<div align="center">

Oleic acid   Oxygen Water

</div>

$$CH_3(CH_2)_7CH(OH)CH(OH)(CH_2)_7COOH$$
<div align="center">9:10-Dihydroxystearic acid</div>
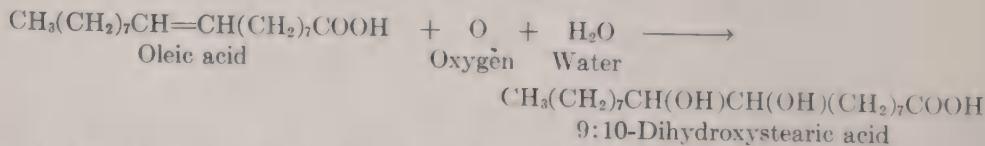
Similarly, linoleic and other diethenoid acids produce tetrahydroxy acids; triethenoid acids produce hexahydroxy acids, etc.

Under properly chosen conditions almost quantitative yields of 9:10-dihydroxystearic acid can be obtained from oleic acid by permanganate oxidation.[11] For the commercial production of hydroxy acids Swern *et al.*[12] have recommended oxidation with performic or peracetic acid, with

[11] See, for example, A. Lapworth and E. N. Mottram, *J. Chem. Soc.*, *127*, 1628–1631 (1925).

[12] D. Swern, G. N. Billen, T. W. Findley, and J. T. Scanlan, *J. Am. Chem. Soc.*, *67*, 1786–1789 (1945).

these acids to be formed *in situ* by the reaction of hydrogen peroxide with formic or acetic acid. In the laboratory experiments 60% of the oleic acid in red oil was converted to 9:10-dihydroxystearic acid by this method.[13]

Under more severe oxidizing conditions, rupture tends to occur at the double bonds:

$$CH_3(CH_2)_7CH=CH(CH_2)_7COOH + 2 O_2 \longrightarrow$$

Oleic acid   Oxygen

$$CH_3(CH_2)_7COOH + HOOC(CH_2)_7COOH$$

Nonanoic acid   Azelaic acid
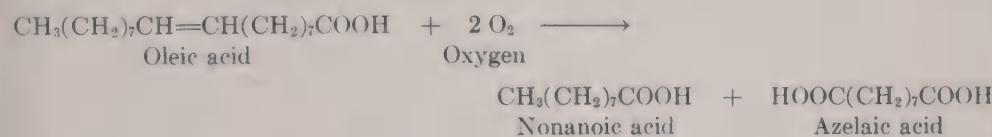
The above reaction, commonly carried out with the aid of ozone or potassium permanganate, is used analytically to locate the position of the double bonds in fatty acids of unknown structure.

Two other useful and widely used analytical methods—the Bertram oxidation method[14] for the determination of total saturated acids, and the Hilditch-Lea method[15] for completely saturated glycerides—depend upon chemical oxidation with potassium permanganate.

It is to be emphasized that chemical oxidation is by no means as straightforward as the above equations would suggest. In each case only the over-all reactions have been indicated; the intermediate reactions are complex and, in fact, not yet completely understood. A great variety of side reactions are possible and in any case oxidation must be carefully controlled to insure a preponderance of the desired products. Among the other compounds which may be obtained are monobasic, dibasic, and hydroxy acids of shorter chain length than are to be expected from the above idealized reactions; and also oxido (epoxy) acids, keto acids, hydroxyketo acids, fatty aldehydes, aldehydo acids, and other fragments, ranging down to water and carbon dioxide.

8. ATMOSPHERIC OXIDATION. RANCIDITY

From a practical standpoint, atmospheric oxidation of fats may be more or less sharply differentiated into that occurring in highly unsaturated oils, which is accompanied by polymerization, and is generally useful, and that occurring in less unsaturated materials, which leads to the development of

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[13] It is to be noted that peracid oxidation produces the low-melting isomer of 9.10-dihydroxystearic acid (m.p. 96°C.), whereas permanganate oxidation yields the high-melting form (m.p. 132°C.).

[14] S. H. Bertram, *Z. deut. Oel Fett-Ind.*, *45*, 733–736 (1925); *Chem. Weekblad*, *24*, 226–229, 320 (1927). For a detailed study of the Bertram method, see T. P. Hilditch and J. Priestman, *Analyst*, *56*, 354–367 (1931); and for a more recent modification, see K. A. Pelikan and J. D. Von Mikusch, *Oil & Soap*, *15*, 149–150 (1938).

[15] T. P. Hilditch and C. H. Lea, *J. Chem. Soc.*, *1927*, 3106–3117.

rancidity,[16] and is the source of most of the spoilage of edible fats and oils. Oxidation of the former type will be covered in a later section, hence the present discussion will be limited to oxidation in relation to rancidity and other types of flavor and odor deterioration in fats.

(a) Mechanism of Rancidification

The initial step in the oxidation of a fat is the addition of oxygen at or near the double bond of a fatty acid chain, to form unstable compounds which are generally designated as peroxides, the reaction according to classical fat chemistry being as follows:

$$
\begin{array}{ccc}
\overset{\displaystyle H}{\underset{\displaystyle |}{}}\ \overset{\displaystyle H}{\underset{\displaystyle |}{}} & & \overset{\displaystyle H}{\underset{\displaystyle |}{}}\ \overset{\displaystyle H}{\underset{\displaystyle |}{}} \\
-C=C- + O_2 & \longrightarrow & -C-C- \\
& & \underset{O-O}{}
\end{array}
$$
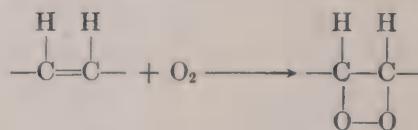
However, Farmer and co-workers[17] have demonstrated that, in the case of nonconjugated fatty acids oxidized at atmospheric temperatures, the initial oxidation products consist of *hydroperoxides*, in which oxygen is combined with a CH_2 group adjacent to an intact double bond.

It was originally postulated by Farmer *et al.* that peroxidation involves simple addition of oxygen to methylene groups. However, it now appears more probable, as suggested by Gunstone and Hilditch,[18] that the initial combination of oxygen is in reality at a double bond, more or less as indicated above, and that hydroperoxides are formed by a rearrangement of the unstable complex produced originally. In the case of oleic acid the reaction may thus be represented as follows:

$$
-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{}{C}}=\overset{H}{\underset{}{C}}-\overset{H}{\underset{}{C}}- + O_2 \longrightarrow -\overset{H}{\underset{H}{C}}-\overset{H}{\underset{O-O}{C}}-\overset{H}{\underset{}{C}}-\overset{H}{\underset{}{C}}- \longrightarrow -\overset{H}{\underset{H}{C}}-\overset{H}{\underset{OOH}{C}}-\overset{H}{\underset{}{C}}=\overset{H}{\underset{}{C}}-
$$

and in linoleic acid:

$$
-\overset{H}{\underset{}{C}}=\overset{H}{\underset{H}{C}}-\overset{H}{\underset{}{C}}-\overset{H}{\underset{}{C}}=\overset{H}{\underset{}{C}}- + O_2 \longrightarrow -\overset{H}{\underset{O-O}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{}{C}}-\overset{H}{\underset{}{C}}=\overset{H}{\underset{}{C}}- \longrightarrow
$$

$$
-\overset{H}{\underset{OOH}{C}}-\overset{H}{\underset{}{C}}=\overset{H}{\underset{}{C}}-\overset{H}{\underset{}{C}}=\overset{H}{\underset{}{C}}-
$$
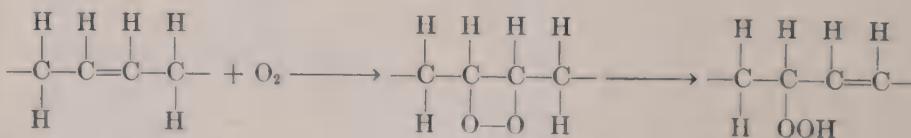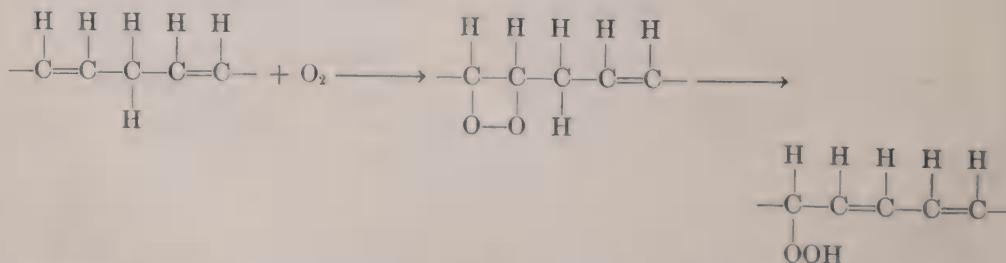
[16] For a general review of the subject of rancidity, see the monograph of C. H. Lea, *Rancidity in Edible Fats*, Department of Scientific and Industrial Research, Food Investigation Report No. 46, H. M. Stationery Office. Also published by Chem. Pub. Co., New York, 1939.

[17] See, for example, E. H. Farmer, G. F. Bloomfield, A. Sundralingam, and D. A. Sutton, *Rubber Chem. Tech.*, 15, 756–764 (1942) and *Trans. Faraday Soc.*, 38, 348–356 (1942). E. H. Farmer and D. A. Sutton, *J. Chem. Soc.*, 1943, 119–122.

[18] F. D. Gunstone and T. P. Hilditch, *J. Chem. Soc.*, 1945, 836–841.

It is to be noted that the above mechanism involves migration of the double bond at the point of oxygen addition. In linoleic or linolenic acid this will lead to the production of conjugated compounds. The development of considerable conjugation concurrently with peroxidation is actually observed to occur; for example, in the oxidation of methyl linoleate at 20°C. Gunstone and Hilditch[18] found diethenoid conjugation rising to a maximum of 22.8%. In polyethenoid acids (linoleic and linolenic) peroxidation is apparently confined to the active CH_2 group situated between two double bonds.[18] According to Hilditch *et al.*,[18,19] the temperature above which hydroperoxide formation ceases to be a dominant factor is approximately 80°C.

Modern theory assumes that oxygen originally attacks the fat additively at but a relatively few points; thereafter, the reaction with oxygen proceeds substitutively by a free radical-activated chain mechanism.[19a] As addition occurs much more readily in fatty acids with a so-called active methylene group, *e.g.*, linoleic or linolenic, it is considered that in commercial fats these acids constitute the focal points from which general oxidation of the fat proceeds.

During the early stages of oxidation (comprising the so-called induction period), the peroxides formed appear to be relatively stable, so that their content increases more or less parallel with the oxygen absorption of the fat. In the later stages, however, they begin to decompose or react with one another or with other products of oxidation, to produce the compounds actually responsible for rancid flavor and odor.

Peroxides are estimated through their ability to liberate iodine from potassium iodide in glacial acetic acid solution. The *peroxide value* of a fat is a measure of its content of reactive oxygen, in terms of millimols of peroxide, or milliequivalents of oxygen, per 1000 grams of fat (1 millimol = 2 milliequivalents). In the United States the method of Wheeler[20] is usually used for the determination of peroxides, whereas in Europe the procedure of Lea[21] or of Taffel and Revis[22] is generally followed.

The typical sharp, unpleasant odor of rancidity is believed to be chiefly due to the presence of aldehydes of medium molecular weight, and particularly heptylic and nonoic aldehydes.[23] Such compounds may be formed by the oxidation and rupture of a fatty acid chain, for example, according to the following scheme:[23a]

[19] D. Atherton and T. P. Hilditch, *J. Chem. Soc.*, *1944*, 105–108.
[19a] E. H. Farmer, *Trans. Inst. Rubber Ind.*, *21*, 122–132 (1945); *Trans. Faraday Soc.*, *42*, 228–236 (1946).
[20] D. H. Wheeler, *Oil & Soap*, *9*, 89–97 (1932). See also R. F. Paschke and D. H. Wheeler, *ibid.*, *21*, 52–57 (1944).
[21] See p. 106 of the monograph of C. H. Lea (footnote 16), and also C. H. Lea, *J. Soc. Chem. Ind.*, *65*, 286–291 (1946).
[22] A. Taffel and C. Revis, *J. Soc. Chem. Ind.*, *50*, 87–91T (1931).
[23] W. C. Powick, *J. Agr. Research*, *26*, 323–362 (1923).
[23a] This scheme is intended to be illustrative only; the actual reactions are doubtlessly much more complex.

$CH_3(CH_2)_7CH{=}CH(CH_2)_7COO - R + O \longrightarrow$
   Oleic acid glyceride

$CH_3(CH_2)_7CHO$ + other oxidation products
Nonoic aldehyde
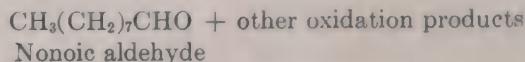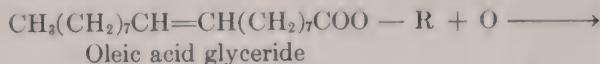
A great variety of other substances, including low molecular weight aldehydes and acids, hydroxy acids, keto acids, ketones, etc., are also found in rancid fats, but it is not believed that any of these contribute in an important way to the flavor or odor of these fats.[23]

Except for the tests for peroxides, mentioned above, most of the chemical tests devised for the detection of rancidity or the estimation of its intensity depend upon the aldehyde content of the fat.[24]   The *Kreis test*, which is qualitative or roughly quantitative, depends upon the presence of a specific class of compounds, namely acetals of epihydrin aldehyde or its homologs. The *Schiff test* is a qualitative test for aldehydes. The quantitative methods of *Issoglio* and *Kerr* depend upon the presence of low molecular weight, steam-volatile aldehydes, whereas that of *Schibsted* is for aldehydes of high molecular weight. The bisulfite method of *Lea* is particularly for the estimation of aldehydes of medium molecular weight.

Although oleic acid oxidizes much less readily than the more unsaturated acids, and lard, hydrogenated shortenings, and similar products exhibit progressively improved stability as their ratio of oleic to more unsaturated acids increases, it is nevertheless probable that the odor and flavor of true rancidity is contributed largely or entirely by oleic acid. The methyl and ethyl esters of oleic acid readily acquire a rancid odor with limited oxidation, whereas pure esters of linoleic and linolenic acid develop relatively little odor after the absorption of large amounts of oxygen, and never develop an odor bearing much resemblance to that of truly rancid fats.[25]   It may be assumed that the readily-formed peroxides of linoleic and other polyethenoid acids catalyze the oxidation of oleic acid, and thus contribute to poor stability in the more highly unsaturated fats.

(b) General Characteristics of Fat Oxidation

When the course of oxidation of a fat is followed experimentally, either by measuring the amount of oxygen absorbed, or determining the peroxide value of the fat, it will be found that the course of oxidation exhibits two distinct phases (see Fig. 1).[25a]   During the initial phase, oxidation proceeds at a relatively slow, and more or less uniform, rate. Then, after a

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[24] For details of the various methods and discussion of their significance, see the monograph of C. H. Lea (footnote 16).
[25] See, for example, G. E. Holm and G. R. Greenbank, *Ind. Eng. Chem.*, 16, 518 (1924).
[25a] R. Gilmont, H. S. Levenson, and L. W. Elder, *Oil & Soap*, 23, 248–252 (1946).

certain critical amount of oxidation has occurred, the reaction enters a second phase characterized by a rapidly accelerating rate of oxidation, and an eventual rate many times greater than that observed in the initial phase. The point at which the sample begins to smell and taste rancid coincides with the beginning or the early part of the second phase. The initial period of relatively slow oxidation of a fat is termed the induction period.
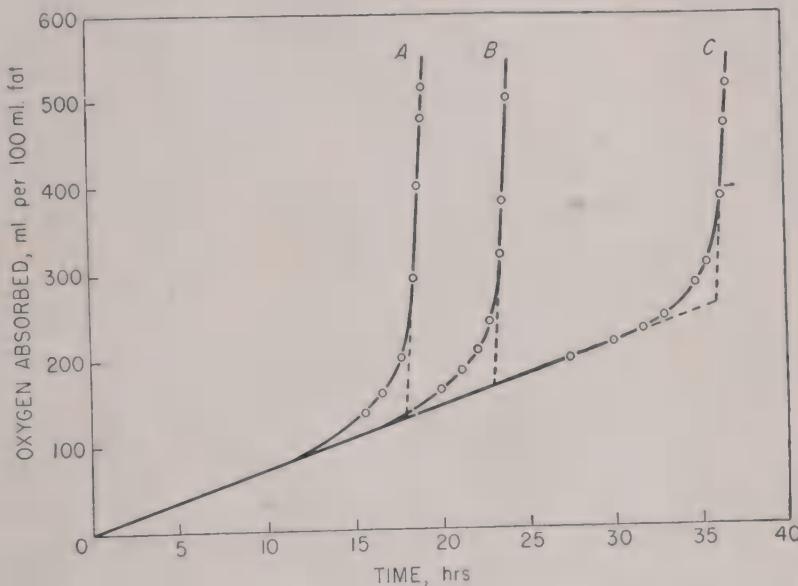
Fig. 1. Oxygen uptake at 90°C. of: (A) corn oil, (B) corn oil plus 0.02% lauryl caffeate, (C) corn oil plus 0.10% lauryl caffeate.[25a]

There is a considerable difference among different fats in the manner in which their oxidation and accompanying flavor deterioration proceeds. The more highly saturated animal fats and hydrogenated oils, whose unsaturated acids consist largely of oleic acid, are relatively little altered in flavor and odor during the early phases of oxidation. The onset of rancidity in such fats is both sudden and definite. On the other hand, relatively unsaturated oils, such as natural cottonseed or soybean oils, exhibit a more gradual deterioration in flavor and odor, and a greater tendency to develop unpleasant flavors and odors different from those of true rancidity. In such oils it is often difficult to determine organoleptically just when rancidity actually begins. Under test conditions which accelerate their rate of oxidation, the more unsaturated oils also absorb more oxygen and develop higher peroxide values before the end of the induction period, and the induction period is somewhat less clearly distinguishable from the later phase of oxidation.

The amount of oxygen which must be absorbed to produce rancidity will

vary considerably according to the composition of the oil, the presence or absence of antioxidants, and the conditions under which oxidation is carried out, but will ordinarily amount to about 15–150% of the oil by volume or 0.02–0.20% by weight. Fats high in oleic acid and low in linoleic or other polyunsaturated acids, will become rancid after the absorption of less oxygen than fats in which the ratio of these acids is reversed.

Most antioxidants, including the tocopherols, cause an increase, not only in resistance to oxidation, but also in the amount of oxidation required to produce rancidity. Thus, for example, lard, which is low in both polyethenoid acids and antitoxidants, will become rancid at 100°C. after it has absorbed about 15–20% of its own volume of oxygen. Hydrogenated vegetable oils (cottonseed, soybean, peanut, etc.) which are similar to lard with respect to unsaturation, but are relatively high in tocopherols, usually become rancid after oxygen adsorption in the range of about 40–80% by volume. Unhydrogenated soybean, corn, or sunflowerseed oils, which are high in both tocopherols and polyethenoid acids, frequently require 150% or more of oxygen to render them rancid.

The peroxide value of a fat at the rancid point likewise tends to be higher the higher the unsaturation of the fat and the higher its antioxidant content. In accelerated oxidation tests at about 100°C. lard, hydrogenated cottonseed oil (shortening), and unhydrogenated cottonseed oil usually begin to exhibit signs of rancidity at peroxide values of about 20, 75, and 125 milliequivalents per kilogram, respectively. However, fats exposed to sunlight or other strong light of short wave length or fats stored with limited access to oxygen, may become rancid at much lower peroxide values than those indicated.

If oxidation is allowed to proceed to an advanced stage the peroxide value will eventually reach a maximum and thereafter decline, as the peroxides begin to decompose or polymerize more rapidly than they are formed. The higher the temperature of oxidation, the lower the maximum peroxide value tends to be; in the purified methyl esters of mixed soybean oil fatty acids Paschke and Wheeler[26] observed maxima of about 3100, 2400, 1700, and 740 milliequivalents per kilogram at 35°, 55°, 75°, and 100°C., respectively. The peroxides are heat-labile, being quickly decomposed at the temperatures employed in steam deodorization, deep frying, etc.

It is doubtless possible for fats to become rancid without more than a very small proportion of their fatty acid chains having undergone scission, for the lower fatty aldehydes are so strong in odor and flavor as to make their presence in traces clearly evident. Thus, for example,

[26] R. F. Paschke and D. H. Wheeler, *Oil & Soap*, **21**, 52–57 (1944).

Pritzker and Jungkunz[27] found that fats containing as little as 0.01% epihydrin aldehyde (and probably other fatty aldehydes to the same order of magnitude) were so rancid as to be inedible. It was estimated that this concentration represented the decomposition of no more than 0.1% of the fat.

In the more advanced stages of oxidation following the end of the induction period, extensive chemical changes occur in an oxidizing fat. These are marked by decreases in the iodine value, the saponification equivalent, and the percentages of normal unsaturated fatty acids, and by the appearance of conjugated acids.[28,29] The changes first mentioned are, of course, occasioned by the splitting of fatty acid chains at their double bonds. The mechanism whereby conjugation is produced has been outlined previously.

In the more advanced stages of oxidation, a considerable amount of polymerization occurs, even at low temperatures.[29a]

(c) Factors Determining Rate of Oxidation

The readiness with which any pure fatty material will oxidize is not measured simply by its over-all degree of unsaturation. On the contrary, ease of oxidation is determined by the distribution, as well as the number, of double bonds. In particular, a single methylene group ($-CH_2-$) between double bonds constitutes a very active center for oxidation. The high reactivity of the isolated methylene group in normal 9:10, 12:13-linoleic acid is responsible for the fact that this acid and its esters oxidize approximately ten times as rapidly as those of oleic acid, which lack such a group. Normal linolenic acid, which contains two active methylene groups, oxidizes about twice as rapidly as linoleic acid. On the other hand, the 9:10, 15:16 isomer of linoleic acid, which has two double bonds but no isolated methylene groups, is relatively resistant to oxidation, bearing more resemblance to oleic acid than to normal linoleic acid in this respect. Conjugated double bonds are very highly reactive toward oxygen, hence elaeostearic acid oxidizes even more readily than linolenic acid. Oleic acid oxidizes more readily than elaidic acid and the natural *cis*- or "alpha" form of elaeostearic acid is more susceptible to oxidation than the higher melting "beta" form[30]; in fact, *cis*-isomers generally undergo addition at the double bond more readily than *trans*-isomers.[31] Geometrical isomerism, therefore, may be presumed generally to have a considerable effect

[27] J. Pritzker and R. Jungkunz, *Z. Untersuch. Lebensm.*, 57, 419–421 (1929).
[28] See, for example, L. J. Filer, Jr., K. F. Mattil, and H. E. Longenecker, *Oil & Soap.* 22, 196–201 (1945).
[29] E. H. Farmer, H. P. Koch, and D. A. Sutton, *J. Chem. Soc.*, 1943, 541–547.
[29a] N. W. Gillam, *Australian Chem. Inst. J. and Proc.*, 15, 150–159 (1948).
[30] J. E. Meyers, J. P. Kass, and G. O. Burr, *Oil & Soap*, 18, 107–109 (1941).
[31] T. Connor and G. F. Wright, *J. Am. Chem. Soc.*, 68, 256–258 (1946).

TABLE 11

RELATIVE RATES OF OXIDATION OF DIFFERENT UNSATURATED FATTY ACIDS

Fatty acid	Chain structure	S, T, & R[a] at 100°C.	M, K, & B[b] at 40°C.	G & H[c] at 20°C.	H & E[d] at 37°C.
Stearic		0.6	—	—	—
Oleic	(cis)	6	—	4	—
Linoleic	(cis) (cis)	64	—	48	42
10:11, 12:13-linoleic	(cis) (cis)	—	—	—	42
Elaidolinolenic	(trans) (trans) (trans)	—	—	—	86
Linolenic	(cis) (cis) (cis)	100	100	100	100
Pseudo-elaeostearic	(trans)	—	123	—	—
Arachidonic	(cis) (cis) (cis) (cis)	—	—	—	199
β-elaeostearic	(trans)	—	196	—	—
α-elaeostearic	(cis)	—	515	—	—

[a] A. J. Stirton, J. Turer, and R. W. Riemenschneider, Oil & Soap, 22, 81–83 (1945).
[b] J. E. Meyers, J. P. Kass, and G. O. Burr, Oil & Soap, 18, 107–109 (1941).
[c] F. D. Gunstone and T. P. Hilditch, J. Chem. Soc., 1945, 836–841.
[d] R. T. Holman and O. C. Elmer, J. Am. Oil Chem. Soc., 24, 127–129 (1947).

on the rate of oxidation, with resistance to oxidation being conferred by isomerization to *trans*-forms.

The relative oxidation rates of pure fatty acid esters, as determined by three different groups of workers, are recorded in Table 11. In this tabulation the various results have been rendered easily comparable by recalculating them to a common basis upon which a value of 100 has been arbitrarily assigned for the oxidation rate of linolenic acid. From the relative rates of oxidation in the series linoleic acid, linolenic acid, arachidonic acid, it will be seen that the addition of each active methylene group beyond one increases the rate of oxidation approximately 100%.

As a consequence of the great disparity in ease of oxidation between oleic acid and the group of acids composed of linoleic acid and linolenic acid, the stability of a hydrogenated vegetable oil is substantially a function of the polyethenoid acid content rather than of the iodine value. Gunstone and Hilditch[32] have observed that the induction period of methyl oleate is halved by the admixture of as little as 1–2% of methyl linoleate.

The stability of commercial hydrogenated fats, in relation to their fatty acid composition, will be discussed at greater length in Chapter VIII.

Fatty acids in the free form appear to oxidize somewhat more readily than when combined in glycerides or other esters. However, the development of a moderate concentration of free acids in a fat does not ordinarily affect its stability to any marked degree. Hydrolysis does not necessarily, or even usually, accompany limited oxidation. Fats in an advanced state of oxidation develop acidity through the accumulation of acidic fission products.

The rate at which oxygen is absorbed is markedly accelerated by heat, and also by exposure of the fat to light, particularly in the ultraviolet or near-ultraviolet regions.[33] The effect of temperature on rates of oxidation, as observed by different workers, is shown graphically in Figure 2. Gunstone and Hilditch,[18] working with purified methyl oleate, observed that the temperature co-efficient of the reaction increased markedly above about 60°C.; below this temperature the rate of oxidation doubled with each increase in temperature of about 45°C., whereas above it the doubling interval was about 11°C. Comparable data on other fatty materials, including commercial fats, are rather limited, but on the basis of available evidence it appears doubtful that they are subject generally to any such effect. The data of Paschke and Wheeler[26] on the purified methyl esters of mixed soybean oil fatty acids indicate a uniform effect of temperature

[32] F. D. Gunstone and T. P. Hilditch, *J. Chem. Soc.*, *1946*, 1022–1025.
[33] See, for example, the following: M. R. Coe and J. A. LeClerc, *Oil & Soap*, *15*, 230–236 (1938); *16*, 146–147 (1939); and *18*, 241–247 (1941); G. R. Greenbank and G. E. Holm, *Ind. Eng. Chem.*, *25*, 167 (1933); *26*, 243 (1934); and *33*, 1058–1060 (1941).

over the range 15–75°C., with a doubling interval of about 12°C. From
accelerated tests on many samples of commercial animal and vegetable
shortenings Mehlenbacher[34] established that the average rate of oxidation
at 110°C. was about 2.5 times that at 97.8°C.; this corresponds to a
doubling interval of 9°C. The results of Thompson[35] on representative
samples of vegetable shortenings stored at 70°F. (21°C.) and 90°F.
(32°C.) and incubated at 145°F. (63°C.) indicate a doubling interval of
approximately 16°C.
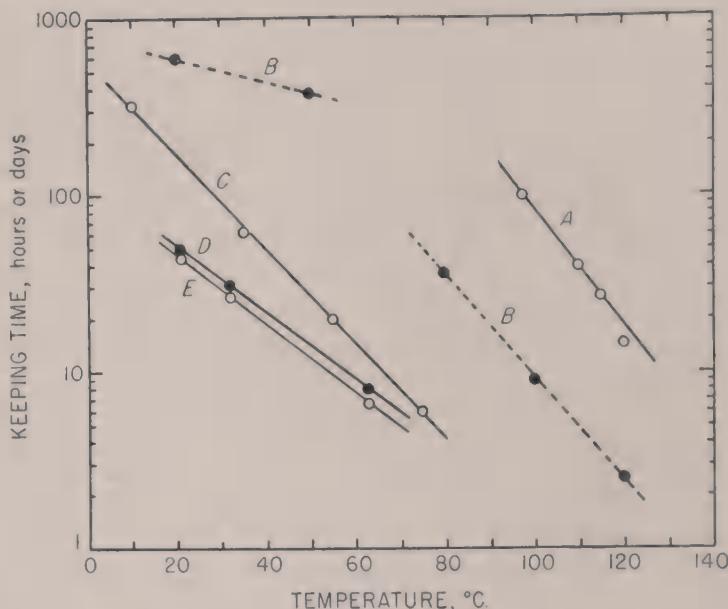
Fig. 2. Effect of temperature increase upon the rate of oxidation of various fats:
(A) miscellaneous commercial animal and vegetable shortenings aerated until
rancid,[34] (B) pure methyl oleate aerated to peroxide value of 500 M.E.,[18] (C) purified
methyl esters of mixed soybean oil fatty acids aerated to peroxide value of 500
M.E.,[20] (D) and (E) commercial vegetable oil shortenings incubated at 63°C. and
stored at 21°C. and 32°C. until rancid.[35]

From the work of Thompson it further appears, however, that the ac-
celerating effect of temperature varies somewhat with different samples
because different natural fats differ with respect to their content of anti-
oxidants and pro-oxidants, and these latter substances are not equally
effective at all temperatures. Samples of shortening prepared from different
lots of oil were quite variable in the ratio of the stability at 145°F. to the
stability at 208°F. However, when series of samples were prepared from
a single lot of oil, but given widely varying degrees of stability by different

[34] V. C. Mehlenbacher, *Oil & Soap, 19,* 137–139 (1942).
[35] S. W. Thompson, *Proceedings of the Committee on Food Research, Conference
on Deterioration of Fats and Oils, Quartermaster Corps Manual 17–7* (1945).

amounts of hydrogenation, the different members of a single series invariably exhibited a consistent ratio between the stabilities at the two temperatures (see Fig. 4 in Section *f*).

Obviously, however, the course of oxidation at ordinary atmospheric temperatures is somewhat different from that at elevated temperatures. Gunstone and Hilditch[18] have called attention to the fact that oxidation at the higher temperatures causes a much greater development of free acidity in oils, from splitting at the double bonds to yield short chain mono- and dicarboxylic acids.

(d) Oxidation of Nonglyceride Constituents

Although the chemical changes occurring in the glycerides during rancidification are of chief interest, the effect of oxidation on the minor constituents of oils are also of some importance. The vitamin E activity of the oil of course diminishes as tocopherols are oxidized, and the end of the induction period corresponds to the beginning of rapid destruction of carotene and vitamin A. Certain interrelationships in the nutritional functions of the two vitamins are now known to be traceable to the protective effect of tocopherols (vitamin E) on vitamin A. As far as is known, oxidation has no effect on most other minor oil components. However, Cattaneo[36] has reported that oxidation to the point of rancidification produces a marked decrease in the percentage of unsaponifiable matter in certain oils. This is attributed to the oxidative rupture of squalene or other unsaturated hydrocarbons to form acidic products.

(e) Antioxidants and Pro-oxidants

While the ease and rapidity with which an oil will oxidize depends primarily upon its content of reactive double bonds, it is also considerably influenced by the presence of certain accessory substances, which may occur in the oil either naturally or adventitiously. Those substances which favor the oxidation of fats are termed pro-oxidants, while those inhibiting oxidation are known as antioxidants or inhibitors. For discussion of the practical uses of antioxidants for the preservation of fats, see Chapter VIII.

All naturally occurring fats and oils contain characteristic antioxidants. In vegetable oils these substances appear to serve the specific purpose of protecting the oil from deterioration during the normal life of the parent seed or fruit. Vegetable oils normally have a larger content of antioxidants than do animal oils, and hence are usually more stable than animal oils of an equivalent degree of unsaturation.

A remarkable characteristic of the antioxidants is their great effective-

[36] P. Cattaneo, *Anales asoc. quím. argentina*, *33*, 110–119 (1945).

ness in low concentrations in the oil. The natural antioxidant content of an oil usually does not amount to more than a few hundredths of 1%.

The generally accepted mechanism by which traces of a foreign material are able to exert a powerful inhibiting effect on oxidation is essentially that first suggested by Christiansen.[37] According to his so-called chain reaction theory, the fat is able to unite with oxygen to form a peroxide only after it is activated by the absorption of energy. After union has occurred and peroxide formation is completed, the activating energy may be released and made available for the activation of a new molecule, to form a new peroxide. A chain of reactions is thus set up, and the initial absorption of a single unit of energy will result in the formation of a great number of peroxide molecules, unless the chain is broken by absorption of the activating energy in an extraneous reaction.

The antioxidants are presumed to be substances which are capable of absorbing the activating energy and thus preventing it from being transmitted to further molecules of the oil, or in other words, which are capable of breaking the reaction chain. If the average chain is normally very long, it will be seen that the presence of even a very small amount of antioxidant may be sufficient materially to reduce its length, with a corresponding reduction in the rate of oxidation. The antioxidant may be expected to be itself oxidized in the process of breaking the chain.

It is possible to free natural fats of their antioxidants by molecular distillation or treatment with suitable adsorbants, and artificial antioxidant-free glycerides or other fatty esters may be prepared from distilled fatty acids or their monoesters. Such purified materials have repeatedly been observed to have little or no induction period, and, when fatty materials have been analyzed for antioxidant content throughout the course of an oxidation experiment, the disappearance of the antioxidant has generally coincided with the end of the induction period.[38] Furthermore, antioxidants clearly have no effect after the end of the induction period; once rapid oxidation has set in, the oxidation rate is as rapid in a fat originally containing antioxidants as in an unprotected fat. From such observations it is generally assumed that any fat exposed to oxygen will resist rancidification for a shorter or longer time simply according to the rate at which its antioxidants are destroyed under the conditions obtaining while it is being stored or tested. Such may be the case in general; however, a sufficient number of anomalies has been noted to cause some doubt that the pattern of antioxidant action is as simple as that outlined above.

[37] J. A. Christiansen, *J. Phys. Chem.*, *28*, 145–148 (1924).
[38] See C. E. Swift, W. G. Rose, and G. S. Jamieson, *Oil & Soap*, *19*, 176–180 (1942); C. Golumbic, *ibid.*, *20*, 105–107 (1943); L. J. Filer, Jr., K. F. Mattil, and H. E. Longenecker, *ibid.*, *22*, 196–201 (1945).

Whereas purified fatty esters high in linoleic or other polyunsaturated acids have no appreciable induction period, some time is required for oxidation to become rapid in corresponding materials in which oleic acid greatly predominates.[39] It appears probable that the considerable induction period of the latter is not, as sometimes supposed, merely the result of inadequate purification.

A phenomenon not easily reconcilable with conventional theories of antioxidant action is the failure in some cases of the antioxidant to disappear by the end of the induction period. Lea[16] mentions certain instances in which this has been observed, and more recently Lovern[40] has reported others, including the oxidation of dried milk powder with ethyl gallate as the antioxidant, and the oxidation of certain carotene solutions in which monoethanolamine served as the inhibitor. That natural fats may become rancid and yet contain either antioxidants or substances easily transformed to antioxidants is evidenced by the fact that ordinarily slightly rancid fats will still exhibit a considerable induction period after their peroxides have been decomposed and their volatile constituents removed by steam deodorization (see Fig. 127, page 769). Emmerie-Engel analyses of lard fortified with gross amounts of tocopherols show appreciable tocopherol contents well after rapid oxidation of the fat has begun.[41] However, in this case it is possible that the indicated tocopherol contents are fictitious.

On the basis of any simple interpretation of the chain reaction theory, the protective action of an antioxidant would be expected to be in direct proportion to its concentration in the fat or other substrate. Such, however, is by no means the case, except, perhaps, within limited ranges with a very few antioxidants. In general, the addition of an antioxidant yields steadily diminishing returns, in terms of stability of the substrate, as the amount added is increased. It is generally assumed that at higher concentrations an appreciable portion of the antioxidant is consumed in side reactions, and thus does not serve its function as a breaker of the main reaction chain. It also appears possible that in some cases decomposition of the antioxidant may yield substances with a pro-oxidant action.

The action of tocopherols, the principal natural antioxidants of fats and oils, is particularly complex. Tocopherols attain their maximum effectiveness at comparatively low levels, roughly equivalent to their natural concentrations in vegetable oils.[42] Above the optimum concentration to-

[39] See, for example, J. E. Meyers, J. P. Kass, and G. O. Burr, *Oil & Soap*, *18*, 107–109 (1941).
[40] J. A. Lovern, *Oil & Soap*, *23*, 40–45 (1946).
[41] G. D. Oliver, W. S. Singleton, and A. E. Bailey, *Oil & Soap*, *21*, 188–193 (1944).
[42] C. Golumbic, *Oil & Soap*, *20*, 105–107 (1943).

copherol concentrates prepared from vegetable oils may actually function as pro-oxidants[41,43] (see Fig. 3).

Prior to the discovery of the tocopherols, a very puzzling feature of antioxidant action was that certain acidic "antioxidants" (citric acid, phosphoric acid, cephalin, etc.) would greatly extend the stability of vege-
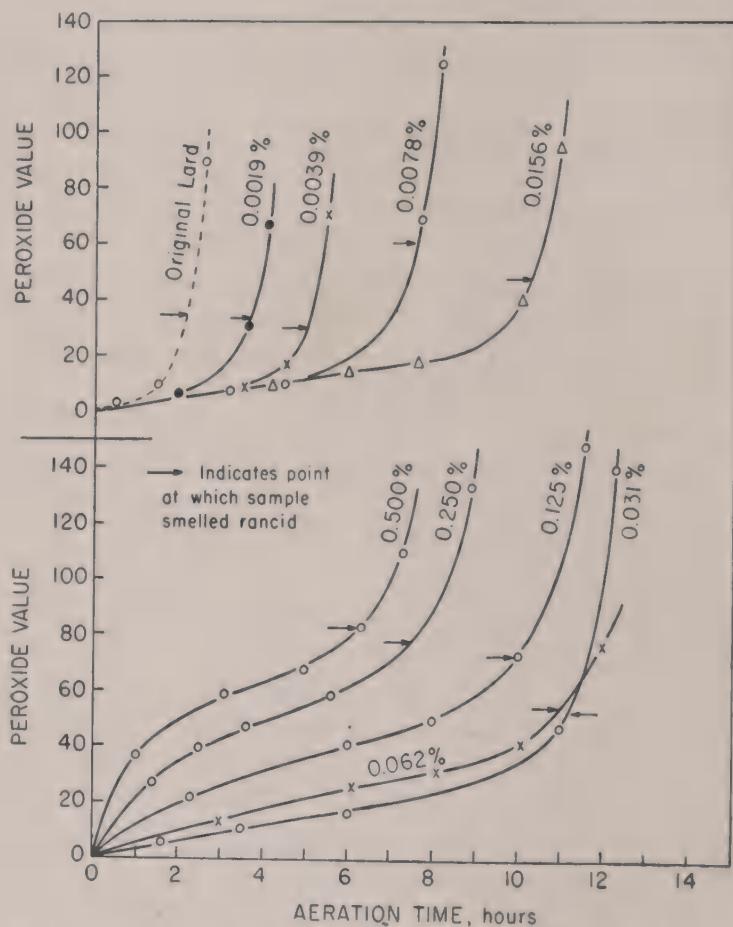
Fig. 3. Stability of lard fortified by the addition of various percentages of mixed tocopherols in the form of a molecular distillate from peanut oil.[41]

table oils, but were relatively impotent in most animal fats and quite impotent in purified fatty substrates. It is now known that such materials are not true antioxidants, but are "synergists," which are capable of enhancing the protective effect of tocopherols or other antioxidants of the phenolic type. The mechanism of their action is still controversial.[43a]

The pro-oxidants most likely to be encountered in commercial fat prod-

[43] A. E. Bailey, G. D. Oliver, W. S. Singleton, and G. S. Fisher, Oil & Soap, 20. 251–255 (1943).
[43a] For a review of synergists, see H. A. Mattill, Oil & Soap, 22, 1–3 (1945).

ucts are metallic soaps, formed through the action of free fatty acids upon tanks and other metallic equipment used in processing or storing oils.

In a series of experiments in which different metal soaps were tested for their effect on the stability of lard at 208°F., King, Roschen, and Irwin[43b] found that the following amounts of metal (p.p.m.) were required to reduce the keeping time of the fat by one-half: copper, 0.05; manganese, 0.6; iron, 0.6; chromium, 1.2; nickel, 2.2; vanadium, 3.0; zinc, 19.6; aluminum, *ca.* 50. It will thus be seen that copper, in particular, is a very strong pro-oxidant, being effective in a concentration of much less than one part per million. Copper and copper-bearing alloys are consequently avoided in the fabrication of equipment for handling edible fats and oils; the use even of brass valves or cocks is considered bad practice in mills and refineries.

From a practical standpoint, the possible harm which a metal may do to the stability of oils depends both upon its pro-oxidant activity *per se,* and the extent to which it may become dissolved in the oil. Materials high in free fatty acids are much more inclined to dissolve metals than are neutral oils. In processing operations carried out at low temperatures common carbon steel does not appear to be sufficiently corroded by oils materially to affect their stability. However, at high temperatures, and particularly at those employed in steam deodorization (400–475°F.), the pro-oxidant effect of traces of metal from the processing vessel may become serious. Ziels and Schmidt[44] have reported a series of tests in which hydrogenated cottonseed oil (shortening) was deodorized in the laboratory at 180–230°C., in glass, with and without the presence of various metals and alloys in the form of granules or turnings. Of all the metallic materials tested, only aluminum and nickel were without some deleterious effect on the oil. Of the various alloys, Inconel and Rezistal were the least injurious and Monel the worst. Stabilized stainless steel (Type 316) was somewhat superior to ordinary (Type 304) stainless steel. The latter was in turn, however, but little better than ordinary boiler-plate steel.

In practice, a film of heat-polymerized oil sometimes forms upon the surface of vessels used for high-temperature processing, and this tends to afford some protection against the pro-oxidant effect of the metal.

Metal strips suspended in oils under test will in some cases accelerate oxidation of the oil without themselves undergoing detectable loss in weight. This has caused some workers to believe that metals may exert a significant catalytic effect without undergoing solution in the oil. However, in view of the extremely small amounts of metal required to affect the stability of oils, this point cannot be regarded as fully established.

[43b] A. E. King, H. L. Roschen, and W. H. Irwin, *Oil & Soap, 10,* 204–207 (1933). See also AOCS Committee on Analysis of Commercial Fats & Oils, *Oil & Soap, 22,* 101–107 (1945).
[44] N. W. Ziels and W. H. Schmidt, *Oil & Soap, 22,* 327–330 (1945).

The mechanism by which metals or other pro-oxidants accelerate the oxidation of fats is still obscure, although the theory has been advanced[16] that they operate principally as catalysts for the destruction of natural antioxidants.

Some of the acidic synergists for fats, e.g., commercial lecithin, citric acid, and phosphoric acid, have the property of inactivating heavy metal pro-oxidants through the formation of metal complexes. It has been suggested[45] that metal deactivation rather than a synergistic effect with tocopherols is actually responsible for their effectiveness. Hills and Conochie[45a] have reported that the pro-oxidant effect which common salt is sometimes observed to have on dry fats is traceable to the presence of magnesium chloride in the salt.

(f) Accelerated Oxidation Tests

To evaluate the stability of fat samples within a reasonable time in the laboratory it is necessary to resort to some means for accelerating their normal rate of oxidation. While it has been suggested that oxidation be hastened by subjecting the sample to strong light or by adding metallic pro-oxidants,[46] both of these methods are difficult to control, and in practice the reaction is almost invariably accelerated by heat.

For routine testing of edible fats the method most employed in the United States is one first suggested by Wheeler[47] and modified and standardized by King, Roschen, and Irwin,[43] and variously referred to as the *aeration test*, the *active oxygen method* (A.O.M.), or the *Swift stability test*. It involves continuously aerating the sample at 208°F. (97.8°C.) and, by periodic titration, determining the time required for a specific peroxide value to develop. Originally, the aeration rate was regarded as critical, but this was later disproved.[48] The peroxide value chosen as the end point should represent an average value for the beginning of definite rancidity in the kind of fat under test; the original method of King *et al.* was designed for lard and a peroxide value (milliequivalents per kilogram) of 20 was suggested. However, there are no generally accepted values for any fats; standards vary from one laboratory to another. For lard, hydrogenated lard shortenings, oleo oil, and hydrogenated vegetable oil shortenings (from cottonseed and soybean oils), McKinney and Jacobson[49] have recommended values of 20, 40, 60, and 80, respectively. A suitable value

[45] See H. J. Dutton, A. W. Schwab, H. A. Moser, and J. C. Cowan, *J. Am. Oil Chem. Soc.*, 25, 385–388 (1948).
[45a] G. L. Hills and J. Conochie, *J. Council Sci. Ind. Research Australia*, 18, 355–365 (1945).
[46] See, for example, H. D. Royce, *Oil & Soap*, 10, 123–125 (1933).
[47] D. H. Wheeler, *Oil & Soap*, 9, 89–97 (1932).
[48] E. Freyer, *Oil & Soap*, 12, 139–144 (1935). L. B. Kilgore and D. H. Wheeler, *ibid.*, 12, 178–180 (1935).
[49] R. H. McKinney and W. Jacobson, *Baker's Digest*, 19, No. 4, 97–99, 112 (1945).

for unhydrogenated olive or peanut oils is about 50–60, whereas cottonseed oil, corn oil, sunflowerseed oil, or soybean oil will usually become rancid at a peroxide value between 125 and 150. In many laboratories, for rapid routine testing, it is customary to record the time required for the effluent air from the sample to develop a rancid odor, without regard to the peroxide value of the fat.

In a modification of the above method due to Mehlenbacher[50] the sample is aerated at 110°C.; the stability at this temperature averages about 40% of that found at 97.8°C. In the *oven* or *Schaal test*[51] the sample is simply incubated, usually at 140° or 145°F., until it develops either a specific peroxide value or organoleptic rancidity.

Somewhat less suitable for rountine use are accelerated methods wherein the oxygen absorption of the sample is measured physically and the stability is determined according to the sudden uptake occurring at the end of the induction period. However, such methods are preferred in some laboratories. For details of suitable apparatus and its use the reader is referred to the publications of Johnston and Frey[52]; Eckey[53]; and Gilmont, Levenson, and Elder.[54]

According to data reported by Thompson,[35] the relationship in vegetable oil shortenings between keeping time in the oven test and keeping time in storage at atmospheric temperatures is as follows: 10 days in the oven at 145°F. is equivalent to: (*a*) one to two months in storage at 70°F., or (*b*) two to four months storage at 90°F.

Thompson has also reported extensive data on the relationship between A.O.M. stabilities at 208°F. and stabilities by the oven method at 145°F. These are shown for typical series of hydrogenated cottonseed and soybean oils in Figure 4. It will be seen that in each individual sample of oil there was a consistent relationship between the stabilities as determined by the two methods, regardless of the degree to which the oil had been stabilized by hydrogenation or the addition of either a phenolic or an acidic antioxidant. Thus, for example, for the cottonseed oil the following equation holds throughout a wide range:

$$A.O.M., \text{ hrs.} = 2 \text{ (oven test, days)} - 5$$

This is in striking contrast to the variability found among samples derived from *different lots* of oil, for which one day by the oven method may correspond to as little as about one hour or as much as about two hours by the A.O.M. Evidently a capacity for responding differently to an increase in the temperature of oxidation is inherent in the untreated oils.

[50] V. C. Mehlenbacher, *Oil & Soap, 19,* 137–139 (1942).
[51] N. T. Joyner and J. E. McIntyre, *Oil & Soap, 15,* 184–186 (1938).
[52] W. R. Johnston and C. N. Frey, *Ind. Eng. Chem., Anal. Ed., 13,* 479–481 (1941).
[53] E. W. Eckey, *Oil & Soap, 23,* 38–40 (1946).
[54] R. Gilmont, H. S. Levenson, and L. W. Elder, *Oil & Soap, 23,* 248–252 (1946).

Since there are no significant differences in glyceride composition among different samples of the same kind of oil, this capacity must be ascribed to the effect of natural anti-or pro-oxidants (see page 59).

In the evaluation of antioxidants or synergists dissimilar to those naturally occurring in fats and oils serious error can arise from the use of
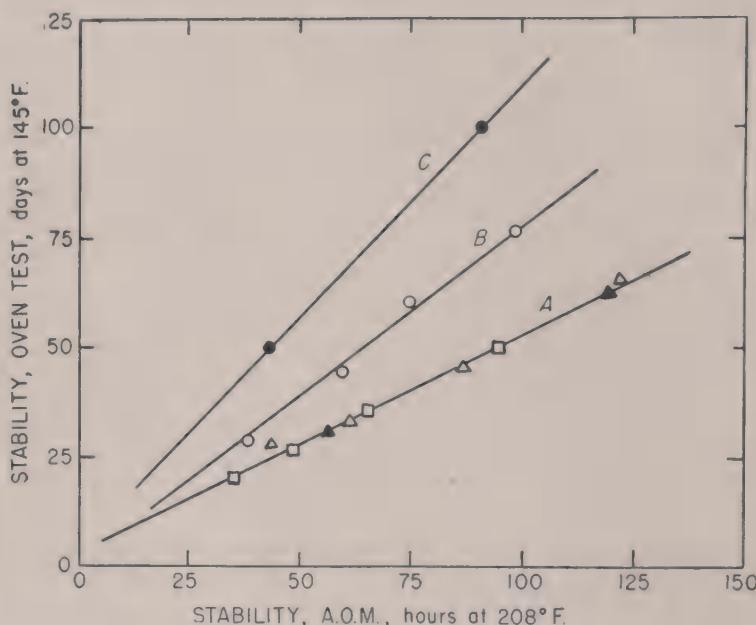
Fig. 4. Stability at 145°F. (oven test) *vs.* stability at 208°F. (A.O.M.) of individual samples of vegetable oil hydrogenated to different degrees: (*A*) cottonseed oil (squares indicate oil alone, open triangles indicate oil plus acidic antioxidant or synergist, closed triangles indicate oil plus phenolic antioxidant); (*B*) soybean oil, sample number 1, with various antioxidants; (*C*) soybean oil, sample number 2, with various antioxidants.[35]

tests wherein oxidation is carried out under conditions far removed from those obtaining in ordinary storage. The following results, reported by Nagy, Vibrans, and Kraybill,[55] are illustrative: When a certain sample of lard was tested by the active oxygen method at 97.8°C. the addition of 0.10% of D-isoascorbyl palmitate was observed to extend the keeping time from 8 to 40 hours. However, when the comparison was carried out by an oxygen absorption method at 70°C., addition of the palmitate was found to *decrease* the keeping time from 35 to 6 hours. The latter result was the one in accordance with storage tests carried out at room temperature.

Inconsistent results such as those detailed above, plus the fact that there are obvious differences in the course by which oxidation proceeds at elevated temperatures, have caused a search for a satisfactory non-

[55] J. J. Nagy, F. C. Vibrans, and H. R. Kraybill, *Oil & Soap*, 21, 349–352 (1944).

heat-accelerated test method, particularly among British workers. The method of Banks,[56] wherein oxidation is carried out at ordinary temperatures, but is accelerated by hematin, appears valuable for the evaluation of antioxidants in pure substrates. However, it is not suitable for the routine testing of commercial fats, since it is erratic when traces of peroxides are initially present in the material under test.

(g) Flavor Reversion

Certain fats, after undergoing refining treatment and being rendered flavorless and odorless by steam deodorization, are inclined to develop objectionable flavors through oxidation far short of that required to produce rancidity. The flavor and odor changes occurring in such fats are commonly termed "flavor reversion."[57] The oils subject to pronounced flavor reversion are those which contain appreciable amounts of linolenic acid or other fatty acids with more than two double bonds. These include all marine oils, linseed oil, soybean oil, and rapeseed oil. The most troublesome case of flavor reversion is that occurring in soybean oil, which —although a linolenic acid oil—is primarily used for edible purposes. Mild reversion of unhydrogenated soybean oil produces a slight "beany" flavor, which in more advanced stages may become "grassy," "painty," or "fishy." Hydrogenated soybean oil acquires a distinctive flavor reminiscent of hay or straw; it has a peculiar latent quality, which is inclined to leave an aftertaste in the mouth long after food containing the oil has been eaten. The flavor and, more particularly, the reverted odor, are unpleasantly accentuated when the fat is heated to high temperatures, as in deep frying. The reverted flavor of linseed oil is similar to that of soybean oil, but is stronger. Marine oils reacquire a fishy flavor and odor upon reversion.

No data are available as to the exact amount of oxygen required to produce flavor reversion in any particular fat subject to this form of deterioration. It is certain, however, that it is generally extremely small—in some cases probably not more than a fraction of one per cent of that necessary for the development of rancidity.

The cause of flavor reversion is at present unknown; efforts of many recent workers to elucidate the mechanism of reversion have yielded directly contradictory results; and altogether this phenomenon may be said to constitute one of the chief puzzles of present day fat chemistry.

As mentioned previously, reversion appears to be associated with the

[56] A. Banks, J. Soc. Chem. Ind., 63, 8–13 (1944).
[57] For reviews of the subject of flavor reversion, see the following: M. M. Durkee, Ind. Eng. Chem., 28, 898–903 (1936); H. E. Robinson and H. C. Black, Ind. Eng. Chem., 37, 217–219 (1945); A. E. Bailey, Oil & Soap, 23, 55–58 (1946); H. C. Black and K. F. Mattil, Chapter XIX, in Soybeans and Soybean Products, K. S. Markley, ed., Interscience, New York, 1950.

presence of linolenic or other highly unsaturated fatty acids. Peculiarly, however, a tendency toward reversion is not eliminated by hydrogenation of an oil to a point where all such acids have disappeared. However, the reverted flavor of a hydrogenated oil usually bears little resemblance to that of the same oil before hydrogenation, and it is probable that reversion is fundamentally different in the two cases.

The reverted flavor of hydrogenated linseed oil (and, by inference, that of soybean oil) has been specifically ascribed by Lemon[58] to the presence of "isolinoleic" (9:10, 15:16-octadecadienoic) acid, produced by hydrogenation of linolenic acid at the middle double bond. Lemon's results have been confirmed by Taylor and co-workers.[59] Both of these groups of workers observed pronounced heat reversion in reconstituted glycerides or other esters which had been purified from unsaponifiable material. On the other hand, no such reversion was observed in cottonseed oil products to which the unsaponifiable matter from soybean oil had been added.[59] Further evidence that ability to revert is a property of the glycerides is provided by the experiments reported by Sanders,[60] in which soybean oil was found to revert even after removal of its unsaponifiable material by extraction, whereas the unsaponifiable material added to cottonseed oil produced no reversion.

On the other hand, Mattil[61] maintains that the unsaponifiable fraction cannot be absolved from involvement in the reversion phenomenon, since he was able to produce reversion in peanut oil by adding unsaponifiable material from soybean oil and greatly to reduce the reverting tendencies of the latter oil by exhaustion of its unsaponifiable material with adsorbents. Neal[61a] claims that the flavor stability of soybean oil is improved by reducing the unsaponifiable content by drastic steam deodorization. Certainly, nitrogenous materials must be involved in the often-observed development of fishy flavors in unhydrogenated vegetable oils. Davies and Gill[62] have shown that fishiness in oils is associated with nitrogenous compounds entering into chemical combination with the oil during the course of oxidation, and that in some cases highly unsaturated fatty acids must be present for fishiness to develop.

It would thus appear that *both* nonglyceride substances and certain unsaturated acids may be involved. Possibly reversion occurs as a result of

[58] H. W. Lemon, *Can. J. Research*, *F22*, 191–198 (1944). See also H. W. Lemon, A. Lips, and W. H. White, *ibid.*, *F23*, 295–303 (1945); H. W. Lemon, *ibid.*, *F25*, 34–43 (1947); H. J. Lips, H. W. Lemon, and G. A. Grant, *ibid.*, *F25*, 44–50 (1947).

[59] S. W. Thompson, W. G. Taylor, and A. R. Gudheim, *Proc. 2nd Conference on Flavor Stability in Soybean Oil*, Soybean Research Council, October 29, 1946. W. G. Taylor, *J. Am. Oil Chem. Soc.*, *26*, 413–418 (1949).

[60] J. H. Sanders, *Proc. Conference on Flavor Stability in Soybean Oil*, Soybean Research Council, April 22, 1946.

[61] K. F. Mattil, *Proc. 2nd Conference on Flavor Stability in Soybean Oil*, Soybean Research Council, October 29, 1946.

[61a] R. H. Neal (to Best Foods, Inc.), U. S. Pat. 2,351,832 (1944).

[62] W. L. Davies and E. Gill, *J. Soc. Chem. Ind.*, *55*, 141–146 (1936).

interaction between the two concurrently with limited oxidation, to pro-
duce compounds which associate themselves tenaciously with each of the
above-mentioned fractions. If this is the case, it is to be expected that im-
purities or variations in processing conditions would influence the degree
to which reversion occurs. It may be that the reversion observed upon
heating the oil is associated with the glyceride composition, whereas that
occurring at ordinary temperatures arises more directly from unsaponifi-
able materials in the oil. Taylor[59] maintains that the ordinary reversion
of flavor and "heat reversion" flavor are entirely different, and that the
confusion of results referred to above arises principally from failure to
distinguish between the two. With this the author can scarcely agree; to
him the disagreeable "aftertaste" of unheated hydrogenated soybean oil
and heated oil appear identical.

Sanders[63] has reported extensive experimental work which supports the
contention that the flavor instability of soybean oil is in direct proportion
to the color of the oil after refining and bleaching treatment. Oils with high
bleach colors, including oil from "field-damaged" beans, may be presumed
to contain comparatively large amounts of substances arising from decom-
position of proteins or other components of the beans, since carotenoid
pigments are removable with relative ease. According to Hutchins,[64] the
moisture content of the beans during milling is an important factor in
determining the tendency of the oil to undergo reversion, since beans of
high moisture content are easily damaged in processing.

Because of their extremely low concentration in the oils, relatively
little progress has been made in the separation and identification of the
compounds specifically responsible for reverted flavor and odor. However,
preliminary work by Daubert and co-workers[62a] identifies as possible
offenders acetaldehyde and 2:4-decadienals in unhydrogenated soybean
oil, and α,β-unsaturated carbonyl compounds in the hydrogenated oil.

Among the variables in oil processing, the following are reported by
Sanders[60] to have an adverse effect on the flavor stability of soybean oil:
inadequate contact between oil and lye in refining, use of a very strong
lye or a high refining temperature, inadequate removal of foots (soap)
after refining, and insufficient bleaching. Sanders also states that the use
of excessively high temperatures in deodorizing is detrimental to the flavor
stability of unhydrogenated (but not hydrogenated) oil, although in the
author's own experience, high-temperature deodorization, if properly con-
ducted, contributes to flavor stability. It may be mentioned that severe
heat treatment during deodorization, presumably to effect some degree of
polymerization of unsaturated constituents of unknown nature, has been

[62a] A. I. Schepartz and B. F. Daubert, *J. Am. Oil Chem. Soc.*, 27, 367–373 (1950).
R. J. Stapf and B. F. Daubert, *ibid.*, 27, 374–377 (1950).
[63] J. H. Sanders, *Oil & Soap*, 21, 357–360 (1944).
[64] R. P. Hutchins, *Oil & Soap*, 22, 165–168 (1945).

used successfully by European processors to improve the flavor and flavor stability of unhardened marine oils.

A number of special hydrogenation techniques have been patented for producing partially hardened soybean oil with a minimum tendency toward flavor reversion.[64a] These may be considered generally of dubious, or at best, only limited value.

American processors have not generally been able to confirm the reported opinion[65] of certain European processors that the flavor stability of soybean oil is improved by unusually thorough water washing to remove phosphatides.[59] Recent investigations of the flavor problem in unhardened soybean oil have emphasized the deleterious effects of traces of heavy metals in the oil, and the use of metal complexing agents or metal scavengers, such as citric acid or sorbitol.[66] Certain American processors have for many years used citric, phosphoric, or tartaric acids as metal scavengers in deodorizing oils, particularly in installations where iron rust may be introduced with the stripping steam, and the practice is probably even older in Europe. A recent series of patents[66a] claims monoalkyl or alkylene esters of citric acid, e.g., monoisopropyl citrate, as antireversion agents.

9. POLYMERIZATION

Concurrently with oxidation at atmospheric temperatures, or without the assistance of oxygen at elevated temperatures, the highly unsaturated fatty acids and their esters will polymerize. The complex and somewhat obscure mechanism of polymerization will be discussed in detail in Chapter XII.

Unlike most of the reactions of fats and other fatty acid derivatives, polymerization is profoundly influenced by the nature of the alcohol with which the fatty acid is esterified. Triglyceride molecules readily combine with one another to form solid, infusible, "three-dimensional" polymers or gels, such as are seen in paint or varnish films. Corresponding esters of dihydric alcohols ordinarily do not gel, but only form viscous liquids or "linear polymers." In esters of monohydric alcohols or in the free acids, polymerization cannot easily be made to pass the dimeric stage. On the other hand, fatty acid esters of alcohols containing more than three

[64a] For a review of these, see J. W. Bodman, E. M. James, and S. J. Rini, Chapter XVII in *Soybeans and Soybean Products*, K. S. Markley, ed., Interscience, N. Y., 1950.
[65] W. H. Goss, *Oil & Soap*, 23, 241–244 (1946). H. J. Dutton, H. A. Moser, and J. C. Cowan, *Proc. Conference on Flavor Stability in Soybean Oil*, Soybean Research Council, April 22, 1946.
[66] H. J. Dutton, A. W. Schwab, H. A. Moser, and J. C. Cowan, *J. Am. Oil Chem. Soc.*, 25, 385–388 (1948); 26, 441–444 (1949).
[66a] R. H. Neal, C. M. Gooding, and H. W. Vahlteich (to Best Foods, Inc.), U. S. Pat. 2,485,631 (1949) and subsequent patents.

hydroxyl groups—as, for example, pentaerythritol—polymerize more readily than triglycerides, *i.e.*, more readily than natural oils.

Polymerization is carried out commercially in the "bodying" of oils for paint and varnish manufacture and in the manufacture of linoleum and other drying oil products. For further treatment of this reaction see Chapter XXII and also the chapters covering the above products.

10. ISOMERIZATION

Oleic acid, which is the *cis*-form of octadecenoic acid, may be converted to elaidic acid, the *trans*-form, by treatment with the oxides of nitrogen or certain other catalysts, including sulfur and selenium. Griffiths and Hilditch[67] have shown that the reverse transformation can also be accomplished, and that, in either case, an equilibrium mixture is obtained containing about two-thirds elaidic acid and one-third oleic acid. *Trans*-isomers of the natural *cis*-forms of linoleic and linolenic acid may be similarly prepared,[68] as presumably can those of other unsaturated acids.

Partial elaidinization of unsaturated fatty acids may also occur in the commercial hydrogenation and sulfonation of oils.

The conjugated acids elaeostearic and licanic isomerize to high-melting (and presumably *trans*-) forms with considerable ease; in fact, there is often some difficulty in maintaining oils which contain these acids (tung and oiticica oils) in a liquid condition through the course of their commercial extraction and storage. Transformation tends to occur when the oil is exposed to strong light, and is rapid under ultraviolet irradiation. Commercial oiticica oil usually solidifies spontaneously after extraction, as does solvent-extracted tung oil. However, these oils are permanently prevented from elaidinizing by being heated to 200–225°C. for a short time.

Isomerization of nonconjugated fatty acids and their esters to conjugated forms can be brought about by treatment with alkali at an elevated temperature.[68a] Alkali isomerization forms the basis of a relatively new and highly important analytical method, as the conjugated compounds absorb light strongly in the ultraviolet regions and are readily estimated spectrophotometrically. The appearance of conjugated acids also invariably accompanies the oxidation of nonconjugated fatty acids or their esters (page 51), and appears to be a necessary preliminary to the polymerization of drying oils (Chapter XXII).

[67] H. N. Griffiths and T. P. Hilditch, *J. Chem. Soc.*, *1932*, 2315–2324; *J. Soc. Chem. Ind.*, *53*, 75–81T (1934).
[68] See J. P. Kass and G. O. Burr, *J. Am. Chem. Soc.*, *61*, 1062–1066 (1939); J. P. Kass, J. Nichols, and G. O. Burr, *ibid.*, *63*, 1060–1063 (1941).
[68a] T. Moore, *Biochem. J.*, *31*, 141–154 (1937). J. P. Kass and G. O. Burr, *J. Am. Chem. Soc.*, *61*, 3292–3294 (1939).

11. REACTIONS OF HYDROXYL GROUPS

Hydroxyl groups may be introduced into fatty acid chains by various means; in castor oil, which contains ricinoleic acid, they are present naturally. In industrial practice, the most important reaction involving the hydroxyl group is the dehydration of castor oil to produce a drying oil with conjugated acids. This process is discussed in Chapter XXII.

Hydroxyl groups in fats are readily acetylated by reaction with acetyl chloride or acetic anhydride in the presence of pyridine, etc.; this reaction constitutes the basis of various analytical methods for the estimation of these groups. The *acetyl value* is defined as the number of milligrams of potassium hydroxide required to neutralize the acetic acid produced by hydrolysis of one gram of acetylated fat. The *hydroxyl number* is the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of one gram of fat. Methods for the estimation of hydroxyl content do not differentiate between hydroxyl groups in the fatty acid chains and those present in mono- or diglycerides; hence partially hydrolyzed fats may exhibit a considerable acetyl value without containing hydroxy acids.

α-Monoglycerides, like other organic compounds containing adjacent hydroxyl groups in a carbon chain, are oxidized by lead tetraacetate or periodic acid, with fissure of the chain between the two hydroxyl groups. Oxidation with the latter reagent forms the basis of the method of Pohle, Mehlenbacher, and Cook[69] for the estimation of monoglycerides in commercial preparations of this material.

D. Preparation of Miscellaneous Fatty Acid Derivatives

1. PREPARATION OF KETONES, ALDEHYDES, AND HYDROCARBONS FROM FATTY ACIDS

When saturated fatty acids are converted to calcium, barium, or magnesium soaps, and the latter are heated to high temperatures under reduced pressure, fatty ketones are produced.

$$\begin{array}{c} CH_3(CH_2)_{16}COO \\ CH_3(CH_2)_{16}COO \end{array} Ca \longrightarrow \begin{array}{c} CH_3(CH_2)_{16} \\ CH_2(CH_2)_{16} \end{array} CO + CaCO_3$$

Calcium stearate   Stearone   Calcium carbonate
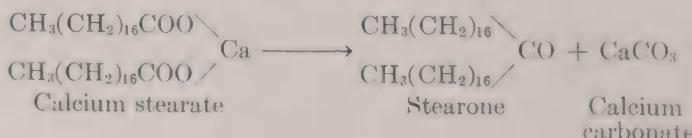
If the soap is heated with the corresponding formate, an aldehyde is produced.

[69] W. D. Pohle, V. C. Mehlenbacher, and J. H. Cook, *Oil & Soap*, 22, 115–119 (1945).

$$\begin{matrix} CH_3(CH_2)_{16}COO \\ CH_3(CH_2)_{16}COO \end{matrix} Ca + \begin{matrix} HCOO \\ HCOO \end{matrix} Ca \longrightarrow 2\ CH_3(CH_2)_{16}CHO + 2\ CaCO_3$$
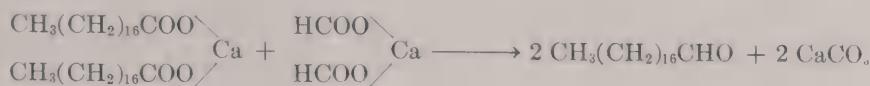
And if the soap is heated with the corresponding hydroxide, the product is a hydrocarbon.

$$\begin{matrix} CH_3(CH_2)_{16} \\ CH_3(CH_2)_{16} \end{matrix} Ca + Ca(OH)_2 \longrightarrow 2\ CH_3(CH_2)_{15}CH_3 + 2\ CaCO_3$$

Soaps of the unsaturated fatty acids undergo similar reactions, but with the production of less of the desired products, from a greater tendency for side reactions to occur. The destructive distillation of soaps of ricinoleic acid[70] or of castor oil[71] yields heptaldehyde and undecenoic acid.

Grün and co-workers[72] have reported high yields of ketones from lauric, myristic, palmitic, stearic, and behenic acids by processing the free acids at *ca.* 300°C. in an iron vessel, with the walls of the vessel serving as a catalyst for the reaction.

2. Pyrolysis to Produce Motor Fuels

In countries lacking supplies of petroleum, particularly in China and Japan, considerable work has been carried out on the pyrolysis of fatty oils, such as tung oil or fish oils, to produce motor fuels (see page 497). In some cases the soaps have been pyrolyzed, whereas in other cases cracking has been carried out directly on the oils.

3. Manufacture of Sebacic Acid

Sebacic acid is produced commercially by the high-temperature (*ca.* 275°C.) decomposition of ricinoleic acid in the presence of water, with an excess of sodium hydroxide acting as a catalyst.

$$CH_3(CH_2)_5CHOHCH:CH(CH_2)_7COOH + 2\ H_2O \longrightarrow$$
$$\text{Ricinoleic acid}$$

$$HOOC(CH_2)_8COOH + CH_3(CH_2)_5CHOHCH_3$$
$$\text{Sebacic acid} \qquad\qquad \text{Octanol}$$
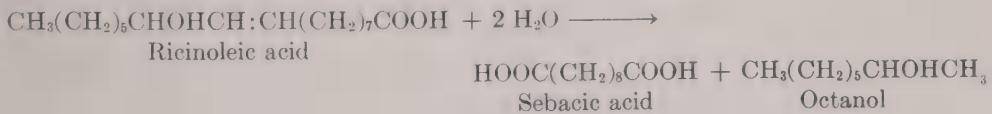
[70] A. A. Vernon and H. K. Ross, *J. Am. Chem. Soc.*, *58*, 2430–2433 (1936).
[71] G. A. Perkins and A. O. Cruz, *J. Am. Chem. Soc.*, *49*, 1070–1077 (1927).
[72] A. Grün, E. Ulbrich, and F. Krczil, *Z. angew. Chem.*, *39*, 421–428 (1926).

PHYSICAL PROPERTIES OF FATS AND FATTY ACIDS

The physical properties of fats are of practical importance for a number of reasons. Many of the technical applications of fatty materials—and in some cases their uses in edible products as well—are dependent upon the oiliness, surface activity, or other physical properties peculiar to long chain compounds. In the manufacture of commercial fat products heat treatment or other purely physical treatment—with or without accompanying phase transformations—is a common adjunct to chemical processing. Recent years have seen physical methods of testing and analysis replace less accurate and more time-consuming chemical methods, and in some cases serve as powerful tools for the extraction of information unobtainable through a strictly chemical approach.

Perhaps the most important group of physical properties consists of those associated with solid–liquid and liquid–solid phase changes, or the process of melting and solidification.[1] Closely related to these changes is the very terminology: *fats and oils*. The term *fat* is ordinarily understood to refer to a material that is solid—the term *oil* to a material that is liquid—at ordinary temperatures. Actually, a fat is virtually never completely solid, and seldom even solidified for the most part. Such common fats as lard, tallow, butterfat, shortening, or margarine are intimate mixtures of a liquid phase with a solid phase consisting of microscopic fat crystals. The plasticity of these products and all other characteristics which distinguish them from liquid oils depend upon the varying proportions of the two phases with changes in temperature.

A. Oiliness and Viscosity

One of the most noticeable characteristics of oils and fats is their "oiliness," or ability to form lubricant films. In this respect, they are quite similar to long chain hydrocarbons. Although the fatty oils have been largely replaced by petroleum products as lubricants for machinery, there are a number of other technical applications in which their primary function is that of lubrication, and even in some edible products their lubricating action is important.

[1] For a complete treatment of these phenomena, see A. E. Bailey, *Melting and Solidification of Fats*, Interscience, New York, 1950.

Oils owe their relatively high viscosities to the long chain structure of their glyceride molecules; hence the viscosity of blown, heat-bodied, or other polymerized oils is much greater than that of normal oils (see pages 898–902). In general, the viscosity of oils decreases slightly with increase in their degree of unsaturation, and oils containing fatty acids of low molecular weight are slightly less viscous than oils of an equivalent degree of unsaturation containing only high molecular weight acids. Rapeseed and other erucic acid oils are a little more viscous than equally unsaturated oils composed of C_{16} and C_{18} acids. Castor oil is in a class by itself with respect to viscosity, being very much more viscous than other oils.
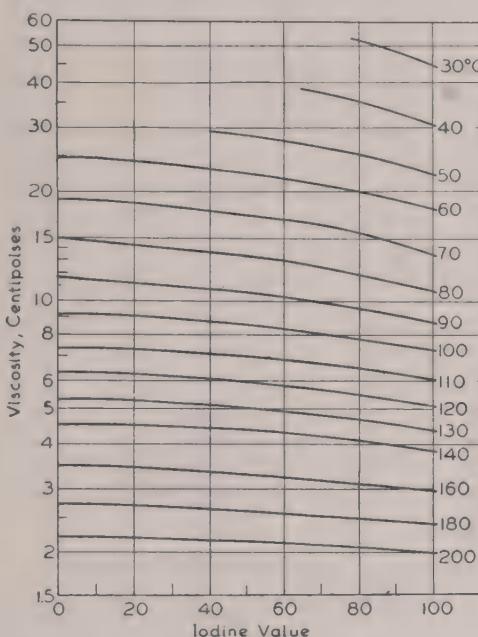
Fig. 5. Viscosity of raw and hydrogenated peanut oil.[3b]

Since viscosity is to some degree dependent upon unsaturation, the viscosity of an oil is increased slightly by hydrogenation (see Fig. 5).

Rescorla and Carnahan[2] have determined the viscosities in both Saybolt and absolute units of a number of oils at 100° and 210°F. Some of their data are shown in Table 11A. Fatty oils change less in viscosity with change in temperature than do mineral oils. The data of Magne and Wakeham[3] (Fig. 5) for raw and hydrogenated cottonseed and peanut oils show the typical behavior of fatty oils. In fats and fatty acids, as in many other liquids, there is, over limited intervals, an approximately linear relationship between the logarithm of the viscosity and the logarithm of the temperature.

[2] A. R. Rescorla and F. L. Carnahan, *Ind. Eng. Chem.*, 28, 1212–1213 (1936).
[3] F. C. Magne and H. Wakeham. (a) *Ind. Eng. Chem.*, 36, 568–570 (1944); (b) *Oil & Soap*, 21, 347–349 (1944).

TABLE 11A

VISCOSITY OF FATS AND OILS[a]

Oil	Acid No.	Sp. gr., 20°/4°C.	Kinematic viscosity, centistokes		Saybolt viscosity	
			100°F.	210°F.	100°F.	210°F.
Almond	2.85	0.9188	43.20	8.74	201	54.0
Olive	—	0.9158	46.68	9.09	216	55.2
Rapeseed	0.34	0.9114	50.64	10.32	234	59.4
Mustard	—	0.9237	45.13	9.46	209	56.9
Cottonseed	14.24	0.9187	38.88	8.39	181	52.7
Soybean	3.50	0.9228	28.49	7.60	134	50.1
Linseed	3.42	0.9297	29.60	7.33	139	49.2
Raw perilla	1.36	0.9297	25.24	6.85	120	47.6
Sunflower	2.76	0.9207	33.31	7.68	156	50.3
Castor	0.81	0.9619	293.4	20.08	1368	97.7
Coconut	0.01	0.9226	29.79	6.06	140	45.2
Palm kernel	9.0	0.9190	30.92	6.50	145	46.5
Lard	3.39	0.9138	44.41	8.81	206	54.2
Neatsfoot	13.35	0.9158	43.15	8.50	200	53.1
Sardine	0.57	0.9384	27.86	7.06	131	48.3
Cod liver	—	0.9138	32.79	7.80	153	50.7
Refined whale	0.73	0.9227	31.47	7.48	147	49.7
Sperm	0.80	0.8829	22.99	5.70	110	44.1

[a] According to A. R. Rescorla and F. L. Carnahan, *Ind. Eng. Chem.*, *28*, 1212–1213 (1936).

Ordinary, fatty oils exhibit the flow behavior of true Newtonian liquids. However, Weltmann[4] has shown that, at very high rates of shear, they may behave as thixotropic plastics, presumably because of the tendency of micelles or other aggregates to become oriented under high shearing stresses. Under such conditions polymerized oils decrease quite markedly in viscosity. In polymerized linseed oils Tollenaar and Bolthof[5] have shown that the decrease is greater the greater the variation in molecular weight of the aggregates in the oil, *i.e.*, it is at a maximum when a non-polymerized oil is mixed with a highly polymerized oil. For the least decrease in viscosity under shear the product must be made by bodying a single oil to the consistency desired, rather than by blending two oils to an intermediate viscosity.

Polymerized oils become less thixotropic as their temperature increases.[4]

Ullock and Badger[6] determined over a wide temperature range the viscosity of a bodied linseed oil which had a viscosity of about 35 poises at the standard temperature of 25°C. (77°F.). The values found were approximately as follows:

[4] R. N. Weltmann, *Ind. Eng. Chem., Anal. Ed.,* *15*, 424–429 (1943); *Ind. Eng. Chem.,* *40*, 272–280 (1948).
[5] D. Tollenaar and H. Bolthof, *Ind. Eng. Chem.,* *38*, 851–853 (1946).
[6] D. S. Ullock and W. L. Badger, *Ind. Eng. Chem.,* *29*, 905–910 (1937).

Temp., °F.	Viscosity, centipoises
77	3500
100	1500
200	150
300	39
400	1.5
500	0.7
600	0.4

Over the range investigated there was a linear relationship between the logarithm of the temperature and the logarithm of the viscosity.

The viscosity of oils is very markedly reduced by the addition of an organic solvent. Viscosity data on mixtures of soybean oil with a commercial petroleum naphtha, consisting largely of hexane (Skellysolve B) with ethylene dichloride, and with trichloroethylene have been published by Johnstone, Spoor, and Goss.[7] Magne and Skau[8] have determined the viscosity of a winterized cottonseed oil at different temperatures, alone and in admixture with various proportions of acetone, 2-butanone (methyl ethyl ketone), and commercial hexane (Skellysolve B).

The viscosities of certain pure triglycerides, as reported by Joglekar and Watson,[9] are recorded in Table 12. The data of Hunten and Maass[10] and of Keffler and McLean[11] on pure fatty acids are given in Table 13. At temperatures not far above their melting points, fatty acids appear to have about one-half the viscosity of the corresponding triglycerides.

TABLE 12

VISCOSITY (CENTIPOISES) OF PURE TRIGLYCERIDES[a]

Temp., °C.	Tricaprin	Trilaurin	Trimyristin	Tripalmitin	Tristearin
40	18.79	—	—	—	—
45	10.06	21.98	—	—	—
60	7.77	13.59	17.71	—	—
70	6.88	10.30	13.42	16.79	—
75	6.25	9.11	11.70	14.67	18.50
80	—	8.09	10.35	12.92	16.21
85	5.51	7.22	9.20	11.44	14.31

[a] R. B. Joglekar and H. E. Watson, *J. Soc. Chem. Ind.*, *47*, 365–368T (1928); *J. Indian Inst. Sci.*, A13, 119–127 (1930).

[7] H. F. Johnstone, I. H. Spoor, and W. H. Goss, *Ind. Eng. Chem.*, *32*, 832–835 (1940).
[8] F. C. Magne and E. L. Skau, *Ind. Eng. Chem.*, *37*, 1097–1101 (1945).
[9] R. B. Joglekar and H. E. Watson, *J. Soc. Chem Ind.*, *47*, 365–368T (1928); *J. Indian Inst. Sci.*, A13, 119–127 (1930).
[10] K. W. Hunten and O. Maass, *J. Am. Chem. Soc.*, *51*, 153–165 (1929).
[11] L. Keffler and J. H. McLean, *J. Soc. Chem. Ind.*, *54*, 178–185T (1935).

TABLE 13

VISCOSITY (CENTIPOISES) OF PURE FATTY ACIDS

Temp., °C.	Oleic[a]	Palmitic[b]	Stearic[b]
20	38.80	—	—
25	27.64	— —	—
30	23.01	—	—
35	19.46	—	—
45	14.08	—	—
60	9.41	—	—
74.0	—	7.17	—
90	4.85	—	—
91.3	—	4.80	—
100.7	—	—	4.56
111.4	—	3.28	—
115.9	—	—	3.43
127.5	—	2.49	—
130.3	—	—	2.67
144.0	—	1.94	—

[a] L. Keffler and J. H. McLean, *J. Soc. Chem. Ind.*, *54*, 178–185T (1935).
[b] K. W. Hunten and O. Maass, *J. Am. Chem. Soc.*, *51*, 153–165 (1929).

B. Surface and Interfacial Tension

Hunten and Maass[10] have reported the surface tensions of the saturated fatty acids from butyric to stearic over a moderate range of temperatures. The surface tension increases with increasing chain length of the acid; at 70°C. their interpolated data for the different members are as follows (dynes per centimeter): C_4, 22.3; C_6, 23.4; C_8, 23.7; C_{10}, 25.2; C_{12}, 26.6; C_{14}, 27.6; C_{16}, 28.2; C_{18}, 28.9. The foregoing do not form an altogether smooth series of values, and it is probable that some of the samples used were rather impure. The surface tension decreases with increasing temperature; the values for butyric acid show the typical slope of the interfacial tension curves: at 8.6°C., 28.0; at 26.5°C., 26.2; at 50.3°C., 23.8; at 73.2°C., 21.7 dynes per centimeter.

The following values were reported for pure fatty acids by Harkins, Brown, and Davis[12]: for caprylic acid at 18.1°C., surface tension, 28.82, interfacial tension against water, 8.22; for ricinoleic acid at 16.0°C., surface tension, 35.81, interfacial tension, 14.25; for oleic acid at 20.0°C., surface tension 32.50, interfacial tension, 15.50 dynes per centimeter.

Values for the surface tension (dynes/cm.) of certain vegetable oils have been given by Halpern[12a] as follows:

[12] W. D. Harkins, F. E. Brown, and E. C. H. Davis, *J. Am. Chem. Soc.*, *39*, 354–364 (1917).
[12a] A. Halpern, *J. Phys. & Colloid Chem.*, *53*, 895–897 (1949).

Temp., °C.	Oil		
	Cottonseed	Castor	Coconut
20	35.4	39.0	33.4
80	31.3	35.2	28.4
130	27.5	33.0	24.0

The interfacial tension of an oil such as cottonseed or peanut oil against water at 70°C. is about 30 dynes/cm.[13]   The interfacial tension, like the
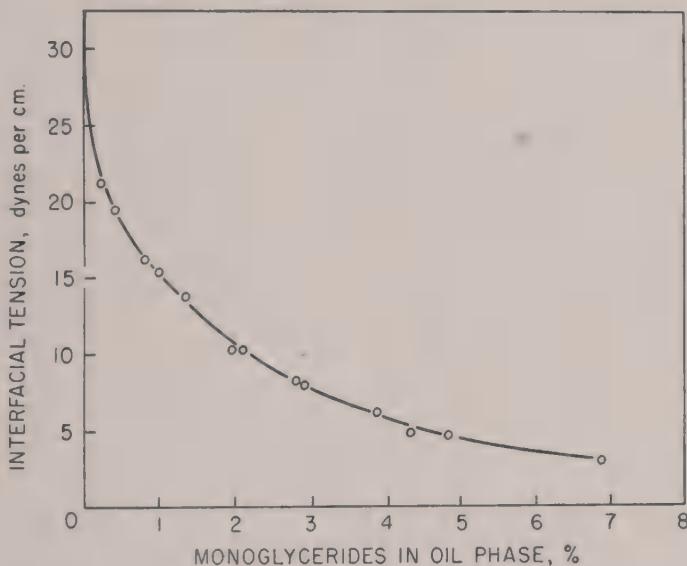
Fig. 6. Interfacial tension against water of refined cottonseed oil containing varying percentages by weight of monoglycerides from partially hydrogenated vegetable oil.[13a]

surface tension, changes relatively slowly with changing temperature. In commercial fats it is greatly lowered by the presence of monoglycerides, and considerably lowered by the presence of free fatty acids or traces of soaps.[13,13a]

Experimental data on surface tensions of fats at higher temperatures do not appear to be available. However, for tripalmitin the following surface tensions are indicated by the correlation of Othmer *et al.*[13b] at 300°C., 12.3 dynes per centimeter; at 250°, 15.7; at 200°, 19.2; at 150°, 22.6; at 100°, 26.3.

Neutral glycerides are relatively lacking in surface activity, and in

[13] R. O. Feuge, *J. Am. Oil Chem. Soc.*, *24*, 49–52 (1947).
[13a] N. H. Kuhrt, E. A. Welch, and F. J. Kovarik, *J. Am. Oil Chem. Soc.*, *27*, 310–313 (1950).
[13b] D. F. Othmer, S. Josefowitz, and A. F. Schmutzler, *Ind. Eng. Chem.*, *40*, 886–889 (1948).

general are much less inclined to be held to solid adsorbents than the various nonglyceride constituents of natural fats and oils. This is taken advantage of in ordinary bleaching of fats and oils by adsorption, and in the various adsorptive methods for the concentration of carotenoids, tocopherols, phosphatides, sterols, etc., from oils. It has been demonstrated, however, that the surface-active properties of glycerides and

TABLE 14

DENSITY OF COMMERCIAL FATS AND OILS[a] (*See text page 82*).

Temp., °F.	Ml./g.	Lbs./ft.[3]	Temp., °F.	Ml./g.	Lbs./ft.[3]
0	0.942	58.8	260	0.848	52.9
10	0.938	58.5	270	0.844	52.6
20	0.934	58.3	280	0.840	52.4
30	0.931	58.1	290	0.837	52.2
40	0.927	57.9	300	0.833	52.0
50	0.923	57.7	310	0.829	51.7
60	0.920	57.4	320	0.826	51.5
70	0.916	57.2	330	0.822	51.3
80	0.913	56.9	340	0.819	51.1
90	0.909	56.7	350	0.815	50.9
100	0.905	56.5	360	0.811	50.6
110	0.902	56.3	370	0.808	50.4
120	0.898	56.0	380	0.804	50.2
130	0.895	55.8	390	0.801	50.0
140	0.891	55.6	400	0.797	49.8
150	0.887	55.4	410	0.793	49.5
160	0.884	55.1	420	0.790	49.3
170	0.880	54.9	430	0.786	49.1
180	0.877	54.7	440	0.782	48.9
190	0.873	54.4	450	0.779	48.6
200	0.869	54.2	460	0.775	48.4
210	0.866	54.0	470	0.772	48.2
220	0.862	53.8	480	0.768	47.9
230	0.858	53.5	490	0.764	47.7
240	0.855	53.3	500	0.760	47.5
250	0.851	53.1	550	0.742	46.3

[a] Figures given are average for cottonseed oil, iodine value about 110.   For other oils containing principally C_{16} and C_{18} fatty acids, make corrections as follows:

Linseed oil, iodine value about 190: to value for ml./g., add 0.013; to value for lbs./ft.[3], add 0.8.

Soybean oil, iodine value about 130: to value for ml./g. add 0.004; to value for lbs./ft.[3] add 0.3.

Hydrogenated vegetable oil or lard, iodine value about 70: from value for ml./g. subtract 0.006; from value for lbs./ft.[3] subtract 0.4.

Highly hydrogenated vegetable oil or other fat, iodine value about 10: from value for ml./g. subtract 0.010; from value for lbs./ft.[3] subtract 0.6.

For other fats and oils of similar composition, make corrections according to the appropriate iodine value.

Note: These values apply only to completely liquid oils, and not to partially solidified materials.

methyl esters as well as fatty acids are such that mixtures of these materials may be resolved by chromatography.[14]

C. Density and Expansibility

1. DENSITY IN THE LIQUID STATE

The density of both fatty acids and glycerides is greater, the lower their molecular weight and the higher their unsaturation. The following expression was developed by Lund[15] for the specific gravity, 15°/15°C., of liquid oils: specific gravity = 0.8475 + 0.00030 (saponification value) + 0.00014 (iodine value). Typical values for the density or specific gravity of different fats and oils are given under the headings of the

TABLE 15

DENSITY AND CHANGE IN DENSITY WITH CHANGE IN TEMPERATURE
PURE LIQUID FATTY ACIDS AND TRIGLYCERIDES

Compound	Density	Change in density per 1°C.
Butyric acid	0.9292 at 50.3°C.[a]	0.00099[a]
Caproic acid	0.8751 at 80.0°C.[b]	0.00089[a]
Caprylic acid	0.8615 at 80.0°C.[b]	0.00079[c]
Capric acid	0.8531 at 80.0°C.[b]	0.00073[c]
Lauric acid	0.8477 at 80.0°C.[b]	—
Myristic acid	0.8439 at 80.0°C.[b]	—
Palmitic acid	0.8414 at 80.0°C.[b]	0.00069[d]
Stearic acid	0.8390 at 80.0°C.[b]	0.00067[d]
Oleic acid	0.8634 at 60.0°C.[e]	0.00068[e]
Tricaprin	0.8913 at 80.0°C.[f]	0.00073[f]
Trilaurin	0.8801 at 80.0°C.[f]	0.00071[f]
Trimyristin	0.8722 at 80.0°C.[f]	0.00069[f]
Tripalmitin	0.8663 at 80.0°C.[f]	0.00067[f]
Tristearin	0.8632 at 80.0°C.[f]	0.00067[f]
Triolein	0.9078 at 25.0°C.[g]	0.00068[g]
Trielaidin	0.8872 at 55.0°C.[g]	0.00069[g]

[a] K. W. Hunten and O. Maass, *J. Am. Chem. Soc.*, *51*, 153–165 (1929).
[b] A. Dorinson, M. R. McCorkle, and A. W. Ralston, *J. Am. Chem. Soc.*, *64*, 2739–2741 (1942).
[c] W. E. Garner and E. A. Ryder, *J. Chem. Soc.*, *127*, 720–730 (1925).
[d] R. F. Ruttan, *Comm. 8th Intern. Congr. Applied Chem. (Appendix)*, *25*, 431–442 (1912).
[e] L. Keffler and J. H. McLean, *J. Soc. Chem. Ind.*, *54*, 178–185T (1935).
[f] R. B. Joglekar and H. E. Watson, *J. Indian Inst. Sci.*, *A13*, 119–127 (1930).
[g] A. E. Bailey and W. S. Singleton, *Oil & Soap.*, *22*, 265–271 (1945).

[14] See, for example, F. T. Walker and M. R. Mills, *J. Soc. Chem. Ind.*, *61*, 125–128 (1942); M. M. Graff and E. L. Skau, *Ind. Eng. Chem., Anal. Ed.*, *15*, 340–341 (1943); and C. E. Swift, W. G. Rose, and G. S. Jamieson, *Oil & Soap*, *20*, 249–250 (1943); H. J. Dutton, *J. Phys. Chem.*, *48*, 179–186 (1944).
[15] J. Lund, *Z. Untersuch. Nahru. Genussm.*, *44*, 113–187 (1922).

individual fats and oils in Chapter VI. Approximate values over an extended range of temperature for any of the common fats containing principally C_{16} and C_{18} fatty acids may be taken from Table 14. Over the range of temperatures to which oils are ordinarily heated in processing, i.e., about 150° to 500°F., the density exhibits a substantially linear variation with temperature, decreasing approximately 0.00064 for each increment in temperature of 1°C., or about 0.000355 for each 1°F.[3]

At lower temperatures the change is greater; for example, about 0.00069 per 1°C. for cottonseed oil between 0 and 40°C.[16]

Density values for certain pure liquid fatty acids and triglycerides are given in Table 15, together with the change in density per unit change in temperature.

2. Density in the Solid State

For various fats chilled to the point of *complete solidification*, Bailey and Singleton[17] have reported the densities, specific volumes, and changes in specific volume with change in temperature; these data are recorded in Table 16. Comparable data for fatty acids do not appear in the litera-

TABLE 16
DENSITY AND THERMAL EXPANSIBILITY OF COMPLETELY SOLID FATS[a]

Fat	Temp., °C.	Density	Sp. vol.	Range, °C.	Change in sp. vol. per 1°C.
Trilaurin, β-form	−38.6	1.057	0.946	−38 to −24	0.00019
Trimyristin, β-form	−38.4	1.050	0.953	−38 to −22	0.00021
Tripalmitin, β-form	−38.2	1.047	0.955	−38 to −18	0.00022
Tristearin, β-form	−38.6	1.043	0.959	−38 to −20	0.00023
Tristearin, β′-form	−38.0	1.017	0.983	−38 to −33	0.00029
Tristearin, α-form	−38.0	1.014	0.987	−38 to −33	0.00032
Trielaidin, highest melting form	−38.7	1.017	0.983	−38 to −22	0.00018
Triolein, highest melting form	−38.7	1.012	0.988	−38 to −33	<0.00038
Hydrog. CSO,[b] highest melting form	−38.2	1.022	0.978	−38 to −20	0.00029
Hydrog. CSO,[c] highest melting form	−38.6	1.000	1.000	−38 to −33	<0.00039
Lard, highest melting form	−38.6	1.005	0.995	−38 to −33	<0.00038

[a] A. E. Bailey and W. S. Singleton, *Oil & Soap*, 22, 265–271 (1945).
[b] Hydrogenated cottonseed oil, I.V. = 0.85; m.p. = 62.5°C.
[c] Hydrogenated cottonseed oil, I.V. = 59.5; m.p. = 41.4°C.

ture. However, unpublished work of the author and associates indicate that the different values are probably not greatly different from those of the corresponding simple saturated triglycerides.

[16] F. C. Magne, E. J. Hughes, and E. L. Skau, *J. Am. Oil Chem. Soc.*, 27, 552–555 (1950).
[17] A. E. Bailey and W. S. Singleton, *Oil & Soap*, 22, 265–271 (1945).

3. DENSITY AND VOLUME OF PLASTIC FATS. DILATOMETRY

At a given temperature, glycerides or fatty acids are considerably more dense in the solid than in the liquid state. Because "solidified" fats ordinarily consist of a mixture of solids and liquid, the density of such fats is not a characteristic comparable to the density of a liquid oil or fat, but is largely dependent upon the relative proportions of the two phases, which sometimes change rapidly with the temperature.
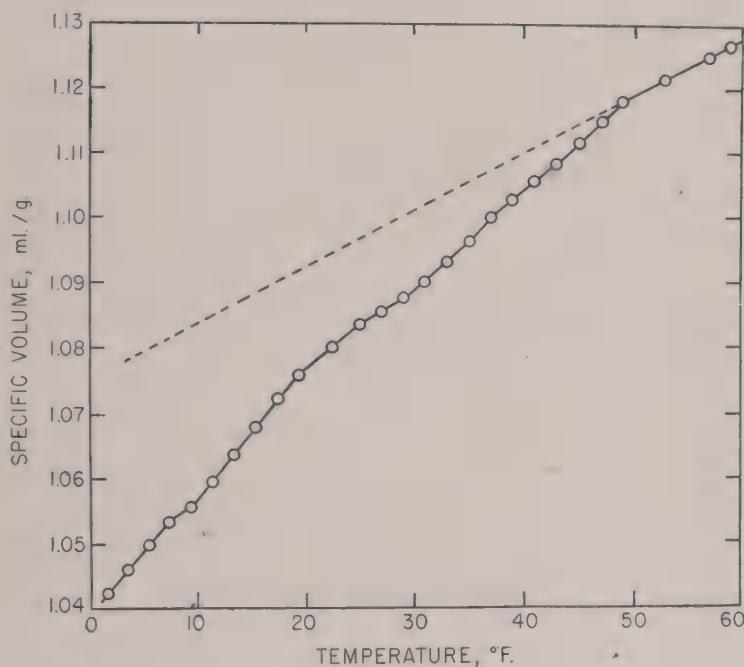
Fig. 7.   Dilatometric curve of a commercial shortening (Crisco).[18]

The systematic investigation of the variation in specific volume of a fat with increase in temperature yields a so-called dilatometric curve, which is indicative of the proportion of solid material at any temperature. The proportion of solids is, in turn, a measure of the consistency of the fat. Dilatometry is used quite extensively for the control of consistency in margarine and shortenings; a typical curve for a commercial shortening (Crisco) is reproduced in Figure 7.[18]

4. DENSITY OF OIL–SOLVENT MIXTURES

The densities of mixtures of soybean oil with petroleum naphtha, ethylene dichloride, and trichloroethylene have been recorded by Johnstone,

[18] W. S. Singleton and A. E. Bailey, *Oil & Soap,* *22*, 295–299 (1945).

Spoor, and Goss.[7]   Magne and Skau[8] have reported values for the density at different temperatures of winterized cottonseed oil mixed in various proportions with petroleum naphtha (Skellysolve B), acetone, and 2-butanone (methyl ethyl ketone). Magne, Hughes, and Skau[16] have reported similar experimental data on mixtures of unwinterized cottonseed oil with methyl pentane, diethyl ether, trichloroethylene, and tetrachloroethylene, together with equations for calculating densities of mixtures of these solvents with other oils.

D. Melting Points

The melting points of fatty acids increase with increasing chain length of the acids, and decrease as the acids become more unsaturated. The melting points of the component fatty acids are reflected in a general way in the melting points of mono-, di-, or triglycerides. Pure fatty acids and triglycerides (and some commercial fats as well) are polymorphic, *i.e.*, they have the property of solidifying in different crystal forms, which are often sufficiently stable to exhibit distinctive melting points, densities, heats of fusion, etc.

TABLE 17

MELTING POINTS OF COMMON FATTY ACIDS AND THEIR MONO-, DI-, AND TRIGLYCERIDES[a]

| Fatty acid | M.p., °C. | | | |
	Free acid	Triglyceride	Diglyceride[b]	Monoglyceride[c]
Butyric	− 7.9	—	—	—
Caproic	− 3.4	−25	—	19.4
Caprylic	16.7	8.3	—	—
Capric	31.6	31.5	44.5	53.0
Lauric	44.2	46.5	56.5	63.0
Myristic	54.4	57.0	65.5	70.5
Palmitic	62.9	65.5	72.5	77.0
Stearic	69.6	73.0	78	81.0
Arachidic	75.3	—	—	84.0
Oleic	16.3	5.5	21.5	35.2
Elaidic	43.7	42	55	58.5
Erucic	33.4	30	46.5	50.0
Linoleic	−6.5	− 13.1	− 2.6	12.3
Linolenic	−12.8	−24.2	−12.3	15.7
Ricinoleic	5.5	—	—	—
Elaeostearic, *cis*	49	—	—	—
Elaeostearic, *trans*	72	—	—	—

[a] Melting point of the highest melting, most stable polymorphic modification is given in all cases.
[b] The symmetrical isomer.
[c] The nonsymmetrical isomer.

Melting points of the most stable (and highest melting) forms of different fatty acids and their glycerides are given in Table 17. For data on the melting points of unstable forms and mixed triglycerides, and the melting characteristics of fat and fatty acid mixtures, reference should be made to other sources.[1,18a]

E. Thermal Properties

1. HEAT OF COMBUSTION

The heats of combustion of the saturated fatty acids increase with increase in the chain lengths of the acids, and vary from about 5900 cal. per gram for butyric acid to about 8900 for lauric, 9600 for stearic, and 9800 for behenic. Values for the unsaturated acids are slightly lower than for saturated acids of the same chain length, about 9450 being recorded for oleic acid, and 9350 for linoleic acid. Triglycerides have substantially the same heats of combustion as the fatty acids of which they are composed, and hence the heat of combustion of common fats, such as lard and tallow, is about 9500 cal. per gram.[19]

Bertram[20] states that the heat of combustion of a variety of fatty oils is expressed closely by the equation:

Heat of combustion = 11,380 — (iodine value) — 9.15 (sap. value)

Calculated values ranged from 9029 for coconut oil to 9680 for rapeseed oil. All the preceding values are expressed in terms of constant volume at 15°C.

2. SPECIFIC HEATS. HEATS OF FUSION OR CRYSTALLIZATION

Garner and co-workers[21] have furnished complete data on the heats of crystallization and specific heats of all the common saturated fatty acids except stearic acid (Table 18). Their work included determinations of the specific heats of both solid and liquid phases near the melting points of the acids; the assumption was made that all the fatty acids were completely solid at temperatures slightly below their melting points. It is now known that even the most carefully prepared fatty acids undergo a significant amount of premelting. Some of the values recorded by Garner et al. for the specific heat of the solid materials are clearly too high, for this reason.

[18a] R. H. Ferguson and E. S. Lutton, *Chem. Revs.*, *29*, 355–384 (1941); E. S. Lutton, *J. Am. Oil Chem. Soc.*, *27*, 276–281 (1950).
[19] See, for example, F. W. Krzywanek, *Biochem. Z.*, *159*, 507–509 (1925).
[20] S. H. Bertram, *Chem. Tech.* (*Dordrecht*), *1*, 101–102 (1946).
[21] W. E. Garner, F. C. Madden, and J. E. Rushbrooke, *J. Chem. Soc.*, *1926*, 2491–2502. W. E. Garner and F. C. Randall, *ibid.*, *1924*, 881–896. W. E. Garner and A. M. King, *ibid.*, *1929*, 1849–1861.

TABLE 18

LATENT HEATS AND HEAT CAPACITIES OF SATURATED FATTY ACIDS[a]

Acid	Latent heat, cal./g.	Specific heats, cal./g.	
		Solid	Liquid
Caproic......	31.2	0.4495 (−33 to −10°C.)	0.5105 (0 to 23°C.)
Caprylic......	35.4	0.4650 (0 to 12°)	0.5050 (18 to 46°)
Capric.......	38.9	0.5009 (0 to 24°)	0.4989 (35 to 65°)
Lauric.......	43.7	0.5116 (19 to 39°)	0.5146 (48 to 78°)
Myristic......	47.1	0.5209 (24 to 43°)	0.5157 (to 84°)
Palmitic......	50.6	0.4920 (22 to 53°)	0.5416 (to 68°)
Arachidic.....	54.2	0.4597 (20 to 56°)	0.5663 (to 100°)
Behenic......	55.1	0.4854 (18 to 71°)	0.5556 (to 109°)
Lignoceric....	57.3	0.4656 (18 to 78°)	0.5855 (to 109°)

[a] According to W. E. Garner, F. C. Madden, and J. E. Rushbrooke, *J. Chem. Soc.*, *1926*, 2491–2502; W. E. Garner and F. C. Randall, *ibid.*, *1924*, 881–896; and W. E. Garner and A. M. King, *ibid.*, *1929*, 1849–1861.

Charbonnet and Singleton[22] have reported values for the heat capacity of trilaurin, trimyristin, tripalmitin, and tristearin in the liquid form and both the α and β modifications of the solid form (except the α-form for trilaurin). Selected values from their work are given in Table 19.

In Table 20 are recorded the heats of fusion and heats of transition determined for the same series of triglycerides.

Oliver and co-workers[23] have published complete thermal data in the range *ca.* −100° to 80°C. for cottonseed oil (iodine value, 108.3), partially hydrogenated cottonseed oil (iodine value, 59.5), highly hydrogenated cottonseed oil (iodine value, 0.85), and a mixture of 52 parts by weight of cottonseed oil with 48 parts of petroleum naphtha (Skellysolve B). Over the range of temperatures covered, the specific heat, C_p, of the completely solid and completely liquid oils could be expressed in terms of the temperature in degrees centigrade, t, by the following equations:

For the liquid oil, 15° to 60°C.:

$$C_p = 0.462 + 0.00061 \, t$$

For the liquid partially hydrogenated oil, 40° to 70°C.:

$$C_p = 0.475 + 0.00055 \, t$$

For the liquid highly hydrogenated oil, 60° to 80°C.:

$$C_p = 0.458 + 0.00097 \, t$$

[22] G. H. Charbonnet and W. S. Singleton, *J. Am. Oil Chem. Soc.*, *24*, 140–142 (1947).
[23] G. D. Oliver, W. S. Singleton, S. S. Todd, and A. E. Bailey, *Oil & Soap*, *21*, 297–300 (1944). A. E. Bailey and G. D. Oliver, *ibid.*, *21*, 300–302 (1944). G. D. Oliver and A. E. Bailey, *ibid.*, *22*, 39–41 (1945).

TABLE 19

SPECIFIC HEATS OF SIMPLE SATURATED TRIGLYCERIDES[a]

Material	Form	Temp., °C.	Specific heat
Trilaurin	Liquid	66.0	0.510
		73.7	0.515
		81.9	0.519
		89.5	0.524
		97.1	0.530
Trimyristin	Liquid	58.4	0.514
		65.3	0.518
		85.3	0.530
		91.9	0.534
Tripalmitin	Liquid	65.7	0.519
		72.8	0.525
		86.8	0.533
		96.0	0.539
Tristearin	Liquid	79.0	0.530
		88.8	0.536
		98.5	0.542
Tristearin	Solid, β-form[b]	−177.3	0.160
		−145.6	0.196
		−116.4	0.224
		− 77.1	0.259
		− 59.6	0.277
		− 30.3	0.310
Tristearin	Solid, α-form[b]	− 81.0	0.273
		− 54.5	0.316
		− 36.5	0.346

[a] G. H. Charbonnet and W. S. Singleton, *J. Am. Oil Chem. Soc.*, 24, 140–142 (1947).
[b] Within the limits of experimental error, values for the same solid form of trilaurin, trimyristin, tripalmitin, and tristearin are identical.

TABLE 20

HEATS OF FUSION AND TRANSITION OF SIMPLE SATURATED TRIGLYCERIDES[a]

Triglyceride	Transformation	Temp., °C.	Heat, cal./g.
Trilaurin	β-form to liquid	46.3	46.2
Trimyristin	β-form to liquid	57.0	50.3
	α-form to liquid	32.3	34.6
	α-form to β-form	32.3	−12.6
Tripalmitin	β-form to liquid	65.7	53.1
	α-form to liquid	44.7	37.4
	α-form to β-form	44.7	−13.3
Tristearin	β-form to liquid	72.5	54.5
	α-form to liquid	54.0	38.9
	α-form to β-form	54.0	−13.7

[a] G. H. Charbonnet and W. S. Singleton, *J. Am. Oil Chem. Soc.*, 24, 140–142 (1947)

For the solvent and liquid oil, 0° to 40°C.:

$$C_p = 0.476 + 0.00065\ t$$

For the solid oil, −100° to −55°C:

$$C_p = 0.442 + 0.00172\ t$$

For the solid partially hydrogenated oil, −80° to −35°C.:

$$C_p = 0.406 + 0.00155\ t$$

For the solid highly hydrogenated oil, −80° to −10°C.:

$$C_p = 0.364 + 0.00135\ t$$

For the solvent and solid oil, −95° to −65°C.:

$$C_p = 0.456 + 0.00108\ t$$

The above values for the solid highly hydrogenated oil refer to oil which had been tempered at a temperature slightly below its melting point, to insure that the sample was in the highest melting crystal modification.

For the unhydrogenated oil, the partially hydrogenated oil, and the highly hydrogenated oil, the heats of fusion were, respectively, 20.6, 27.4, and 44.3 cal. per gram.

Similar equations, published by Ward and Singleton[23a] for peanut oil (iodine value, 94.0) and selectively hydrogenated peanut oil (iodine value, 62.5), are as follows:

For the liquid oil, 27° to 57°C.:

$$C_p = 0.4914 + 0.0004\ t$$

For the solid oil, −163° to −33°C.:

$$C_p = 0.5042 + 0.00195\ t$$

For the liquid hydrogenated oil, 47° to 77°C.:

$$C_p = 0.4715 + 0.00117\ t$$

For the solid hydrogenated oil, −189° to −43°C.:

$$C_p = 0.4418 + 0.00159\ t$$

Heats of fusion for the unhydrogenated and the hydrogenated oils were found to be 21.7 and 24.7 cal. per gram, respectively.

By a different technique from that employed by the above workers, Gudheim[24] found values ranging from 45 to 52 cal. per gram for the heat

[23a] T. L. Ward and W. S. Singleton, J. Am. Oil Chem. Soc., 27, 423–426 (1950).
[24] A. R. Gudheim, Oil & Soap, 21, 129–133 (1944).

TABLE 21. SPECIFIC HEATS OF VEGETABLE OILS[a]

| Temp. | | | | Temp. | | |
°C.	°F.	Sp. heat		°C.	°F.	Sp. heat
Hydrogenated cottonseed oil (Iodine value 6.5)				Tung oil		
79.6	175.3	0.520		21.5	70.7	0.435
119.8	247.4	0.544		37.3	99.1	0.463
160.4	320.7	0.570		79.3	174.7	0.486
201.4	394.5	0.584		120.5	248.9	0.515
219.4	426.9	0.595		160.3	320.5	0.535
270.3	518.5	0.643		190.6	375.1	0.549
Castor oil (Iodine value 83.0)				Linseed oil (Iodine value 172.1)		
29.9	85.8	0.495		30.2	86.4	0.463
79.8	176.7	0.539		70.7	159.8	0.491
120.9	249.6	0.565		110.4	230.7	0.510
172.4	342.3	0.588		150.2	302.4	0.537
209.8	409.6	0.603		191.1	376.0	0.554
219.7	427.5	0.595		240.1	464.2	0.591
250.7	483.3	0.633		270.5	518.9	0.636
271.2	520.2	0.657				
Perilla oil (Iodine value 186.2)				Soybean oil (Iodine value 128.3)		
6.4	43.5	0.414		1.2	34.2	0.448
36.9	98.4	0.436		38.6	101.5	0.469
79.9	175.8	0.454		80.4	176.7	0.493
151.5	304.7	0.481		130.9	267.6	0.526
199.6	391.3	0.515		172.3	342.1	0.558
270.4	518.7	0.575		209.6	409.3	0.590
				240.2	464.4	0.617
				271.3	520.3	0.666

[a] P. E. Clark, C. R. Waldeland, and R. P. Cross, *Ind. Eng. Chem.*, *38*, 350–353 (1946).

TABLE 22. SPECIFIC HEATS OF FATTY ACIDS AT ELEVATED TEMPERATURES[a]

Temp., °C.	Stearic	Lauric	Oleic
10.....................	—	—	0.462
50.....................	—	0.513	0.489
100....................	—	0.543	0.549
150....................	0.585	0.596	0.638
200....................	0.660	0.674	—
250....................	0.775	0.776	—

[a] E. L. Lederer, *Allgem. Oel- u. Fett-Ztg.*, *27*, 237 (1930).

of fusion of various highly hydrogenated vegetable oils. Jack and Brunner[25] have estimated the heat of fusion of butterfat as 19.5 cal. per

[25] E. L. Jack and J. R. Brunner, *J. Dairy Sci.*, *26*, 169–177 (1943).

gram. This is probably a minimum figure, however; the data of Oliver *et al.* would indicate that the value taken by these workers for specific heat of the solid (0.500) was probably influenced by premelting.

TABLE 23

HEAT CONTENTS (Btu. PER POUND) OF FATS AND FATTY ACIDS ABOVE ARBITRARILY CHOSEN TEMPERATURES

Temp., °F.	Cottonseed oil[a]	Partially hydrog. cottonseed oil[b]	Highly hydrog. cottonseed oil[c]	Tallow fatty acids[d]
−148	0.0	—	—	—
−120	8.4	—	—	—
−100	14.2	—	0.0	—
− 94	—	0.0	—	—
− 80	20.1	4.6	5.7	—
− 60	26.8	11.1	11.3	—
− 40	33.3	17.5	17.3	—
− 30	36.6	20.8	20.4	—
− 20	43.5	24.6	23.6	—
− 10	48.0	28.8	26.9	—
− 5	50.3	31.0	28.5	—
0	56.6	33.0	30.2	—
10	69.2	37.6	33.9	—
20	83.0	44.0	37.8	—
30	92.4	53.5	41.0	—
40	99.3	63.5	44.9	0.0
50	106.7	72.4	48.9	6.0
60	113.8	82.0	53.2	12.3
70	117.8	92.0	57.7	19.0
80	123.6	102.0	62.8	27.2
90	128.5	111.2	67.7	36.8
100	133.4	119.2	72.5	49.2
110	138.3	127.2	77.7	67.0
120	143.2	133.2	83.8	72.8
130	148.1	138.0	93.7	78.6
140	153.0	144.3	116.8	84.4
160	162.8	154.4	175.8	96.0
180	—	—	186.5	—
200	—	—	197.4	—

[a] From data of G. D. Oliver, W. S. Singleton, S. S. Todd, and A. E. Bailey, *Oil & Soap*, *21*, 296–300 (1944). Iodine value of the oil = 108.3.
[b] From the data of G. D. Oliver *et al.*; see above. Iodine value of the oil = 59.5.
[c] From the data of G. D. Oliver and A. E. Bailey, *Oil & Soap*, *22*, 39–41 (1945). Iodine value of the oil = 0.85.
[d] Calculated from the data of H. M. Abbott and A. P. Lee, *Oil & Soap*, *15*, 265–268 (1938).

Most published determinations of the specific heat of oils at high temperatures have been of a low order of accuracy. Among the more satis-

factory data thus far reported are those of Clark, Waldeland, and Cross,[26] selected portions of which are recorded in Table 21. The values of Lederer[27] for certain fatty acids at high temperatures are in Table 22.

For engineering calculations it is often convenient to know the heat required to raise a fat from one given temperature to another, without regard to the proportions of sensible heat and heat of fusion in the total heat involved. Table 23 gives the difference in heat content between different temperatures for cottonseed oil, partially hydrogenated cottonseed oil, and highly hydrogenated cottonseed oil, according to Oliver and co-workers[23] and mixed tallow fatty acids according to the data of Abbott and Lee.[28]

The available thermal data on fats and fatty acids, plus certain known characteristics common to all materials, point to the following generalizations:

(a) In the solid state there is but little change in the specific heat of saturated fatty acids or their simple glycerides, as the chain length varies. However, there is a progressive increase in specific heat with increase in the degree of unsaturation. Unstable polymorphic forms of the glycerides have higher specific heats than corresponding more stable forms. In any case, the specific heat of the solid is less than that of the liquid at the same temperature.

(b) The specific heat of liquid fatty acids or glycerides increases with chain length, but decreases as the fat becomes more unsaturated. In both the solid and liquid states there is a progressive increase in specific heat as the temperature increases.

(c) The heat of fusion in both fats and fatty acids is higher the greater the chain length and the lower the unsaturation. In general, mixed glycerides have lower heats of fusion than comparable simple glycerides.

3. Vapor Pressure. Heat of Vaporization

Lederer[29] has calculated from vapor pressure data the following for the heats of vaporization of certain acids at atmospheric pressure:

Acid	Cal./g.	Acid	Cal./g.
Capric	85	Palmitic	58.5
Lauric	68.5	Stearic	56
Myristic	67.5	Oleic	57

At 100 mm. pressure, the above values are about 20% higher; at 5 mm.

[26] P. E. Clark, C. R. Waldeland, and R. P. Cross, *Ind. Eng. Chem.*, *38*, 350–353 (1946).
[27] E. L. Lederer, *Allgem. Oel- u. Fett-Ztg.*, *27*, 237 (1930).
[28] H. M. Abbott and A. P. Lee, *Oil & Soap*, *15*, 265–268 (1938).
[29] E. L. Lederer, *Seifensieder-Ztg.*, *57*, 67–71 (1930).

pressure, they are about 40% higher. Mills and Daniels,[30] from commercial distillation data at 430–440°F. and 7–10 mm. pressure, calculated the heat of vaporization of grease fatty acids to be 107–109 Btu. per lb., and of red oil (commercial oleic acid) to be 124 Btu. per lb.

Complete data on the vapor pressures or boiling points of saturated acids containing from 6 to 18 carbon atoms as reported by Pool and Ralston[31] are recorded in Table 24. For the vapor pressures of fatty acids with more than 18 carbon atoms, see page 881. The boiling points of unsaturated acids appear to be slightly lower than those of saturated acids with the same number of carbon atoms.

TABLE 24

BOILING POINTS OF THE SATURATED ACIDS[a]

Pressure, mm.	Boiling point, °C.						
	Caproic	Caprylic	Capric	Lauric	Myristic	Palmitic	Stearic
1	61.7	87.5	110.3	130.2	149.2	167.4	183.6
2	71.9	97.9	121.1	141.8	161.1	179.0	195.9
4	82.8	109.1	132.7	154.1	173.9	192.2	209.2
8	94.6	121.3	145.5	167.4	187.6	206.1	224.1
16	107.3	134.6	159.4	181.8	202.4	221.5	240.0
32	120.8	149.2	174.6	197.4	218.3	238.4	257.1
64	136.0	165.3	191.3	214.6	236.3	257.1	276.8
128	152.5	183.3	209.8	234.3	257.3	278.7	299.7
256	171.5	203.0	230.6	256.6	281.5	303.6	324.8
512	192.5	225.6	254.9	282.5	309.0	332.6[b]	355.2[b]
760	205.8	239.7	270.0	298.9	326.2[b]	351.5[b]	376.1[b]

[a] W. O. Pool and A. W. Ralston, *Ind. Eng. Chem.*, *34*, 1104–1105 (1942).
[b] Values obtained by extrapolation.

At pressures of 2–20 mm. Norris and Terry[32] have reported that the boiling point of methyl oleate is 3.5°C. lower than that of methyl stearate, while the boiling point of methyl linoleate is similarly 3.5° lower than that of methyl oleate; doubtless, equivalent differences exist in the boiling points of the free acids. These workers were able to effect a partial separation of the stearate and the oleate by use of an efficient laboratory fractionating column, but were unsuccessful in separating the oleate and the linoleate, presumably because of association of the latter.

Terry and Wheeler[32a] found that at low pressures alkali-isomerized linoleic acid had a boiling point about 10°C. higher than normal linoleic acid; hence the former could be concentrated by fractional distillation.

Limited data are available on the vapor pressures of fatty acids in

[30] V. Mills and R. C. Daniels, *Ind. Eng. Chem.*, *26*, 248–250 (1934).
[31] W. O. Pool and A. W. Ralston, *Ind. Eng. Chem.*, *34*, 1104–1105 (1942).
[32] F. A. Norris and D. E. Terry, *Oil & Soap*, *22*, 41–46 (1945).
[32a] D. E. Terry and D. H. Wheeler, *Oil & Soap*, *23*, 88–90 (1946).

binary mixtures. Measurements in the system lauric acid–myristic acid were made at 4 mm. pressure by Monick et al.,[33] and this system and also myristic acid–palmitic acid and palmitic acid–stearic acid were investigated at the same pressure by Williams and Osburn.[33a] In all three systems the more volatile of the two acids exhibited an appreciable negative deviation from ideality, i.e., its vapor pressure was lower than calculated from Raoult's law, whereas the vapor pressures of the less volatile acid corresponded approximately to ideal behavior.

Measurements of the vapor pressures of a number of synthetic mixed triglycerides and of soybean oil and olive oil (purified by molecular distillation) have been made by Perry et al.[34] Representative values found by these workers, in terms of temperatures (°C.) corresponding to specified pressures (mm. of mercury) were as follows:

Fat	0.050 mm.	0.001 mm.
Trilaurin	244	188
Trimyristin	275	216
Tripalmitin	298	239
Tristearin	313	253
Myristopalmitostearin	297	237
Symmetrical oleodistearin	315	254
Soybean oil	308	254
Olive oil	308	253

In a number of other mixed saturated triglycerides, the vapor pressure was found to be essentially a function of the molecular weight. In all cases there was a linear relationship between the logarithm of the vapor pressure and the reciprocal of the absolute temperature, over the range of temperatures and pressures investigated.

The vapor pressure of monoglycerides is a great deal higher than that of triglycerides; the following approximate values have been reported by Ross and co-workers:[35]

Monoglyceride	Pressure, mm.	Temp., °C.
Monocaprin	1	175
Monolaurin	1	186
Monomyristin	1	199
Monopalmitin	1	211
Monostearin	0.2	190
Mono-olein	0.2	186

Vapor pressure data on diglycerides are not available.

[33] J. A. Monick, H. D. Allen, and C. J. Marlies, *Oil & Soap*, *23*, 177–182 (1946).
[33a] F. C. Williams and J. O. Osburn, *J. Am. Chem. Soc.*, *26*, 663–668 (1949).
[34] E. S. Perry, W. H. Weber, and B. F. Daubert, *J. Am. Chem. Soc.*, *71*, 3720–3726 (1949).
[35] J. Ross, A. C. Bell, C. J. Arrowsmith, and A. I. Gebhart, *Oil & Soap*, *23*, 257–259 (1946).

4. Heats of Mixing

Mixing an organic solvent with an oil usually causes an absorption of heat. However, with certain solvents, including particularly chlorinated compounds, the net effect of mixing is an evolution of heat. Johnstone, Spoor, and Goss[7] reported the following changes in temperature upon mixing equal volumes of soybean oil and various solvents at 25°C.:

Solvent	Temp., °C.
Hexane (Skellysolve B)	−0.86
Ethylene chloride, $C_2H_4Cl_2$	−1.44
Ethylene trichloride, $CHCl:CCl_2$	+1.72
Ethyl alcohol, C_2H_5OH	−1.28
Chloroform, $CHCl_3$	+3.61
Carbon tetrachloride, CCl_4	+0.44
Acetone, $(CH_3)_2CO$	−3.00
Benzene, C_6H_6	−0.67
Ethylene tetrachloride, $CCl_2:CCl_2$	+0.22
Phenylacetylene, $C_6H_5:CH$	+0.89

Rough experiments carried out by Skau[36] indicate that petroleum naphtha (Skellysolve B) and cottonseed oil mixed at 25°C. have a maximum negative heat of solution of the order of 2 cal. per gram of mixture, the maximum heat effect occurring with a mixture of about 60 weight per cent or 12 mole per cent of oil, and corresponding to about 3.5 cal. per gram on the basis of the oil.

5. Thermal Conductivity

Fats are relatively poor conductors of heat. For olive oil, Davis[37] has recorded thermal conductivity values, cal./sec./cm.²/°C./cm., of 0.00040 at 19°C. (66°F.) and 0.000385 at 71°C. (160°F.). These correspond, respectively, to 0.097 and 0.093 Btu./hr./ft.²/°F./ft. The data of Kaye and Higgins[38] indicate values, in Btu./hr./ft.²/°F./ft., of 0.104 for castor oil at 68°F., 0.100 for castor oil at 212°F., 0.097 for olive oil at 68°F., and 0.095 for olive oil at 212°F.

F. Smoke, Fire, and Flash Points

The smoke, fire, and flash points of a fatty material are measures of its thermal stability when heated in contact with the air. The smoke point[39] is the temperature at which decomposition products are evolved in suffi-

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[36] E. L. Skau, *private communication* (1944).
[37] A. H. Davis, *Phil. Mag.*, *47*, 972–975 (1924).
[38] G. W. C. Kaye and W. F. Higgins, *Proc. Roy. Soc.*, *A117*, 459–470 (1928).
[39] The smoke point, as commonly recorded, refers to the temperature at which smoking is first detectable in a laboratory apparatus protected from drafts and provided with special illumination. The temperature at which the material smokes freely is usually somewhat higher.

cient quantity for them to become visible; the flash point is the tempera-
ture at which these products are evolved at such a rate that they are
capable of being ignited but not of supporting combustion; and the fire
point is the temperature at which they will support continued combustion.

Fatty acids are much less stable than glycerides, hence the smoke, fire,
and flash points of ordinary oils are dependent principally upon their con-
tent of free fatty acids. The smoke point of an oil such as cottonseed
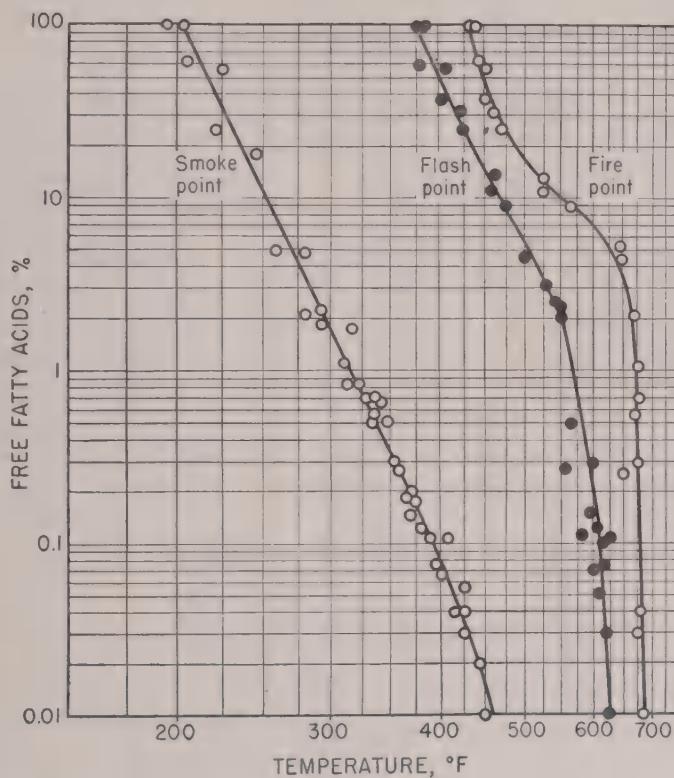
Fig. 8. Smoke, fire, and flash points of miscellaneous
crude and refined fats and oils, as functions of the content
of free fatty acids.

oil or peanut oil varies from about 450°F. at a free fatty acid content of
0.01% to about 200°F. at a free acid content of 100%. Flash points of
these oils exhibit a corresponding variation of from about 625° to 380°F.,
and the variation of the fire point is from about 685° to 430°F. In Figure
8 are detailed data for different oils, taken in part from unpublished re-
sults of the author, and in part from the publication of Morgan.[40]

The degree of unsaturation of an oil has little if any effect upon its
smoke, fire, or flash points. However, coconut oil or other oils containing

[40] D. A. Morgan, *Oil & Soap*, 19, 193–198 (1942).

acids of low molecular weight, have lower smoke, fire, and flash points than ordinary oils of equivalent free fatty acid content.

G. Solubility and Miscibility

1. MISCIBILITY WITH ORGANIC SOLVENTS

At temperatures above their melting points, both fats and fatty acids are freely miscible with a wide variety of hydrocarbons, esters, ethers, ketones, etc. Incomplete miscibility with an organic liquid is, in fact, exceptional. Out of 250 solvents tested by Bills[41] with coconut oil, cod liver oil, linseed oil, olive oil, and butterfat, there were but 28 which were not completely miscible with all five fats when mingled in equal proportions by volume, at room temperature.

Because of the free hydroxyl group in ricinoleic acid, castor oil is distinctive among other oils in its miscibility with organic solvents. At atmospheric temperatures it is incompletely miscible with straight chain hydrocarbons, although its miscibility increases with increasing temperature. It mixes freely with aromatic solvents.[42]

Near their critical temperatures and pressures, organic solvents exhibit an anomalous behavior with respect to their miscibility with fats, *e.g.*, liquid propane becomes incompletely immiscible, and may be used as an agent for liquid–liquid extraction (Chapter XXI).

2. SOLUBILITY IN ORGANIC SOLVENTS[1]

The solubility of a substance in a nonaqueous system depends primarily upon the melting point and heat of fusion of the solute, and secondarily upon those characteristics of the solvent which determine the degree of mutual affinity of solvent and solute molecules. In the so-called *ideal solution*, in which molecules of the solvent and solute have for each other an attraction neither greater nor less than for molecules of their own kind, the solubility at any temperature can be calculated directly from the above-mentioned thermal properties of the solute. In most real solutions, due to a lessened attraction between species of unlike molecules, there is *positive deviation* from ideality, with the solubility at any given temperature being *less* than that in an ideal solution.

When solubilities are calculated in terms of the *mole fraction* of the solute in the solution, a plot of the logarithm of the ideal solubility against the reciprocal of the absolute temperature yields a straight line. Real solubility curves are also often plotted in this way, since in many cases.

[41] C. E. Bills, *J. Biol. Chem.*, 67, 279–285 (1926).
[42] G. H. Taber and D. R. Stevens, *Ind. Eng. Chem.*, 20, 1185–1186 (1928).

even with considerable deviation from ideality, there is an approximation to linearity, particularly in the lower ranges of solubility.

In general, fatty compounds exhibit quite marked positive deviation from ideality in organic solvents; the solubility curve for palmitic acid in acetone shown in Figure 9, constructed from the data of Ralston and
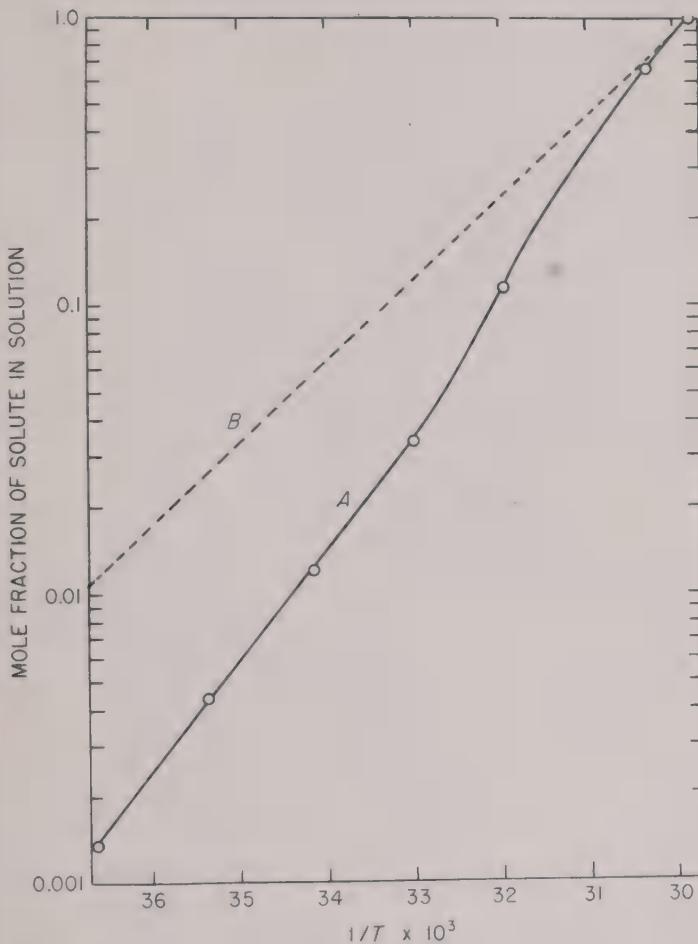
Fig. 9. Solubility of palmitic acid in acetone: (A) actual solubility curve, (B) ideal solubility curve.

Hoerr,[43] may be considered more or less typical. It should be mentioned that the intersolubilizing effect of one fatty acid on another is often considerable; hence solubility data on pure fatty acids are not even approximately applicable to mixtures of fatty acids in solution.

There are sufficient differences in the solubilities of saturated fatty acids (C_{16} and C_{18}), oleic acid, and linoleic and other polyethenoid acids, to permit reasonably efficient separation of mixtures to be made by

[43] A. W. Ralston and C. W. Hoerr, *J. Org. Chem.*, 7, 546–555 (1942).

fractional crystallization, although in all cases limitations are imposed by the existence of eutectics. In commercial fat products trisaturated glycerides are sufficiently less soluble than di- and monosaturated glycerides or triunsaturated glycerides to permit their approximate determination by fractional crystallization from acetone at 30°C.[43a]

For exposition of the theory of solubility and solubility data on individual fatty compounds and their mixtures, reference should be made to the standard texts on the subject.[1,44]

3. Mutual Solubility of Fats and Fatty Acids with Water

The solubility at low temperatures of water in a number of the saturated fatty acids has been determined by Hoerr, Pool, and Ralston.[45] Over the

TABLE 25

Solubility of Water in Fatty Acids[a]

Fatty acid	Temp., °C.	Water dissolved, %
Caproic	−5.4	2.21
	12.3	4.73
	31.7	7.57
	46.3	9.70
Heptylic	−8.3	2.98
	42.5	8.98
Caprylic	14.4	3.88
Monylic	10.5	3.45
Capric	29.4	3.12
Undecylic	26.8	2.72
	57.5	4.21
Lauric	42.7	2.35
	75.0	2.70
	90.5	2.85
Tridecylic	40.8	2.00
Myristic	53.2	1.70
Pentadecylic	51.8	1.46
	90.0	1.62
Palmitic	61.8	1.25
Heptadecylic	60.4	1.06
Stearic	68.7	0.92
	92.4	1.02

[a] According to C. W. Hoerr, W. O. Pool, and A. W. Ralston, *Oil & Soap, 19*, 126–128 (1942).

range of temperatures covered, there was in each case a linear relationship between the temperature and the per cent of water dissolved. The solubility data are given in detail in Table 25. At high temperatures and pres-

[43a] C. A. Coffey and H. T. Spannuth, *Oil & Soap, 17*, 216–217 (1950).
[44] J. H. Hildebrand and R. L. Scott, *Solubility of Non-Electrolytes*, 3rd ed., Reinhold New York, 1950.
[45] C. W. Hoerr, W. O. Pool, and A. W. Ralston, *Oil & Soap, 19*, 126–128 (1942).

sures both fats and fatty acids dissolve large amounts of water. According to the data of Mills,[46] at 450°F. 100 parts of tallow fatty acids dissolves about 9 parts of water, and 100 parts of coconut oil fatty acids dissolves about 20 parts of water, whereas the two become completely miscible with water in all proportions at 610°F. and 560°F., respectively. Allen et al.[47] state that in the range 200–500°F. the solubility of water in tallow fatty acids is given approximately by the relationship:

$$Y = 0.0354 \ t - 3.52$$

where Y = weight per cent of water, and t = temperature,°F. The same authors give the solubility of coconut oil fatty acids in water at 450–475°F. as about one-tenth that of water in the fatty acids. At high temperatures water is said to be slightly less soluble in neutral fats than in fatty acids. The rapidity with which fats hydrolyze at high temperatures of course precludes the accurate determination of the solubility in a neutral fat.

Hoerr et al. also determined the effect of dissolved water on the solidification points of the fatty acids. In a typical experiment, lauric acid containing 2.88% water was observed to have a solidification point 1.14°C. below that of the pure acid.

TABLE 25A

SOLUBILITY (GRAMS PER 100 CC. SOLUTION) OF SATURATED FATTY ACIDS IN WATER AT DIFFERENT TEMPERATURES (°C.)[a]

No. of C atoms	30°	40°	50°	60°
8	0.0789	0.0843	0.0943	0.1071
9	0.0212	0.0222	0.0264	0.0299
10	0.0064	0.0072	0.0081	0.0100
11	0.00198	0.0023	0.0026	0.0032
12	—	0.00077	0.00092	0.00116
14	—	—	0.00042	0.00056

[a] D. N. Eggenberger, F. K. Broome, A. W. Ralston, and H. J. Harwood, J. Org. Chem., 14, 1108–1110 (1949).

The solubility of water in winterized cottonseed oil at ordinary temperatures was determined by Parsons and Holmberg.[48] The water dissolved amounted to 0.071% at 30°F. and 0.141% at 90°F., with a linear relationship obtaining between temperature and water dissolved at intermediate temperatures.

Eggenberger and co-workers[49] have recently reported data on the solubilities of saturated fatty acids containing 8 to 14 carbon atoms in water

[46] V. Mills (to Procter & Gamble Co.), U. S. Pat. 2,156,863 (1939). See also V. Mills and H. K. McClain, Ind. Eng. Chem., 41, 1982–1986 (1949).
[47] H. D. Allen, W. A. Kline, E. A. Lawrence, C. J. Arrowsmith, and C. Marsel, Chem. Eng. Progress, 43, 459–466 (1947).
[48] L. B. Parsons and C. O. Holmberg, Oil & Soap, 14, 239–241 (1937).
[49] D. N. Eggenberger, F. K. Broome, A. W. Ralston, and H. J. Harwood, J. Org. Chem., 14, 1108–1110 (1949).

in the range 30–60°C., which are shown in Table 25A. The solubilities found by Eggenberger *et al.* were in general much lower than those reported previously by Ralston and Hoerr.[43]

4. Solubility of Gases in Fats

The solubilities of air, oxygen, nitrogen, hydrogen, and carbon dioxide in lard, corn oil, and hydrogenated cottonseed oil were determined at 23–26°C. and at 43–47°C. by Vibrans.[50] Schaffer and Haller[51] reported measurements of the solubility of the same gases in lard, cottonseed oil, and butterfat at 40° and 60°C. Parsons and co-workers[52] have determined the solubilities of nitrogen, oxygen, hydrogen, carbon monoxide, and

Table 26

Solubility of Gases in Fats[a]

Fat	Temperature °C.	Solubility coefficient, vol. gas/1 vol. oil				
		N_2	H_2	CO	O_2	CO_2
Cottonseed oil (I.V. = 104.3)...	30.5	0.0711	0.0463	—	—	—
	49.6	0.0779	0.0540	—	—	—
	78.2	0.0891	0.0673	0.1201	—	—
	101.5	0.0976	0.0783	0.1285	—	—
	147.8	0.1183	0.1024	0.1470	—	—
Lard (I.V. = 70.1)............	41.5	0.0765	0.0521	0.1051	—	—
	73.2	0.0879	0.0658	0.1205	—	—
	111.3	0.1038	0.0850	0.1349	—	—
	147.3	0.1206	0.1035	0.1490	—	—
Hydrogenated lard (I.V. < 1)..	64.3	—	0.0614	—	—	0.920
	67.0	0.0844	—	0.1154	0.1450	—
	84.7	—	—	—	0.1535	—
	88.0	—	—	—	—	0.791
	139.4	0.1168	0.0979	0.1460	—	0.619

[a] According to L. B. Parsons, *private communication* (1938).

carbon dioxide in both unhydrogenated and hydrogenated lard and cottonseed oil at temperatures ranging generally from about 30° to 150°C. Since only the latter workers employed a precise experimental technique and covered an extensive range of temperature, their results alone will be quoted here in detail. The values listed in Table 26 represent selected portions of their data. All values in this table are in terms of Ostwald solubility coefficients, *i.e.*, volumes of gas dissolving at 760 mm. pressure in a unit volume of oil, the volumes of both gas and oil being measured at the temperature in question.

[50] F. C. Vibrans, *Oil & Soap, 12,* 14–15 (1935).
[51] P. S. Schaffer and H. S. Haller, *Oil & Soap, 20,* 161–162 (1943).
[52] L. B. Parsons, *private communication* (1938).

It was found that the solubility coefficients, S, were substantially the same for all the fats investigated and could be expressed in terms of the temperature in degrees C., t, by the following linear equations:

$$S_{H_2} = 0.0295 + 0.000497\,t$$
$$S_{N_2} = 0.0590 + 0.000400\,t$$
$$S_{O_2} = 0.1157 + 0.000443\,t$$
$$S_{\cdot o} = 0.0890 + 0.000400\,t$$

The data of Vibrans are in quite close agreement with those of Parsons, but the values reported by Schaffer and Haller are somewhat out of line with those of the other workers. The latter noted an increase in the solubility of hydrogen in butterfat at 60° as compared with 40°C., but reported a decrease in solubility with increased temperature in the case of the other gases. However, the results of Parsons clearly indicate that all of the gases except carbon dioxide are increasingly soluble in the fat as the temperature is raised. Following are typical data, on the absolute solubility of nitrogen in cottonseed oil:

Temperature, °C.	Grams gas dissolved per 100 grams fat (760 mm.)
30.5	0.00888
49.6	0.00929
78.2	0.00985
101.5	0.01029
147.8	0.01151

At 40°C. Schaffer and Haller found all the gases to be 10% to 20% more soluble in butterfat than in lard or cottonseed oil.

From the data of Ouellet and Dubois[52a] it appears that carbon dioxide and possibly other gases are slightly less soluble in fatty acids than in glycerides.

H. Optical Properties

1. Refractive Index

The refractive index of fats has always been a subject of much interest, because of the close relation of this characteristic to the average molecular weight and degree of unsaturation of these materials, and the ease and rapidity with which it may be determined. It is a useful characteristic for quickly sorting oils of unknown identity, and for observing the progress of catalytic hydrogenation. Recently it has been much used, instead of the saponification value, for the analysis of binary mixtures of distilled fatty acid esters.

Values for the refractive indices of various pure fatty acids and glycer-

[52a] C. Ouellet and J. T. Dubois, *Can. J. Research*, B26, 54–58 (1948).

TABLE 27

REFRACTIVE INDICES (n_D) OF FATTY ACIDS AND GLYCERIDES AT 60°C.[a]

Caproic acid	1.4012	Stearic-palmitic-myristic	1.4436
Caprylic acid	1.4125	Stearic-lauric-myristic	1.4422
Capric acid	1.4210	Stearic-capric-myristic	1.4417
Lauric acid	1.4267	Stearic-palmitic-lauric	1.4430
Myristic acid	1.4310	Stearic-myristic-lauric	1.4420
Palmitic acid	1.4347	Stearic-capric-lauric	1.4407
Stearic acid	1.4375		
		Stearic-palmitic-capric	1.4422
Oleic acid	1.4449	Stearic-myristic-capric	1.4413
Elaidic acid	1.4430	Stearic-lauric-capric	1.4405
Linoleic acid	1.4550		
Linolenic acid	1.4640	Oleic-lauric-lauric	1.4456
		Lauric-oleic-lauric	1.4459
Capric-capric-capric	1.4370		
Lauric-lauric-lauric	1.4402	Oleic-palmitic-palmitic	1.4480
Myristic-myristic-myristic	1.4428	Palmitic-oleic-palmitic	1.4476
Palmitic-palmitic-palmitic	1.4452		
		Oleic-stearic-stearic	1.4494
Stearic-stearic-stearic	1.4471	Stearic-oleic-stearic	1.4485
Oleic-oleic-oleic	1.4548	Caproic-oleic-oleic	1.4516
Linoleic-linoleic-linoleic	1.4645	Caprylic-oleic-oleic	1.4505
Linolenic-linolenic-linolenic	1.4741	Capric-oleic-oleic	1.4499
		Lauric-oleic-oleic	1.4498
Stearic-lauric-lauric	1.4437	Myristic-oleic-oleic	1.4505
Lauric-stearic-lauric	1.4442	Palmitic-oleic-oleic	1.4511
		Stearic-oleic-oleic	1.4524
Stearic-palmitic-palmitic	1.4467		
Palmitic-stearic-palmitic	1.4471	Elaidic-lauric-lauric	1.4445
		Lauric-elaidic-elaidic	1.4494
Capric-stearic-stearic	1.4444		
Stearic-capric-stearic	1.4453	OH-capric-OH	1.4443
		OH-lauric-OH	1.4462
Lauric-stearic-stearic	1.4448	OH-myristic-OH	1.4480
Stearic-lauric-stearic	1.4460	OH-palmitic-OH	1.4499
		OH-stearic-OH	1.4515
Palmitic-stearic-stearic	1.4463		
Stearic-palmitic-stearic	1.4475	Oleic-OH-lauric	1.4472
		Oleic-OH-myristic	1.4484
Stearic-myristic-palmitic	1.4437	Oleic-OH-palmitic	1.4495
Stearic-lauric-palmitic	1.4429	Oleic-OH-stearic	1.4507
Stearic-capric-palmitic	1.4423		

[a] Values for the saturated fatty acids are taken from A. Dorinson, M. R. McCorkle, and A. W. Ralston, *J. Am. Chem. Soc.*, *64*, 2739–2741 (1942). Values for the unsaturated acids are from T. R. Wood, F. L. Jackson, A. R. Baldwin, and H. E. Longenecker, *J. Am. Chem. Soc.*, *66*, 287–289 (1944). Values for the saturated simple glycerides are from R. B. Joglekar and H. E. Watson, *J. Indian Inst. Sci.*, *A13*, 119–127 (1930). Values for triolein and trilinolein are from D. H. Wheeler, R. W. Riemenschneider, and C. E. Sando, *J. Biol. Chem.*, *132*, 687–699 (1940). Values for the mixed glycerides and trilinolenin are taken from the publications of C. G. King, B. F. Daubert, *et al.*

ides are recorded in Table 27. To permit intercomparison, these values have all been calculated to a common temperature of 60°C., using the correction factor of 0.00038 per degree C., in converting from other tempera-

tures. Numerous workers have shown that this is approximately the average decrease in the refractive index occasioned by increasing the temperature of fats or fatty acids by 1°C.[52b]

The data in the table illustrate the following generalizations regarding the relationship between the refractive index and the structure and composition of fatty acids and glycerides:

(a) The refractive indices of both fats and fatty acids increase with increase in the length of the hydrocarbon chains and the number of double bonds in the chains.

(b) The refractive indices of simple glycerides are considerably higher than those of the corresponding fatty acids.

(c) The refractive indices of mixed glycerides are in general close to those of corresponding mixtures of simple glycerides.

(d) The refractive indices of monoglycerides are considerably higher than the refractive indices of the corresponding simple triglycerides.

However, there are a few well-marked deviations from these rules. In completely saturated glycerides containing two fatty acids, the symmetrical glycerides are slightly higher in refractive index than their unsymmetrical isomers. Unsymmetrical dioleins containing saturated acids of low molecular weight are abnormally high in refractive index.

The presence of conjugated double bonds in the fatty acids causes a marked exaltation of the refractive index. The presence of hydroxyl groups, as in ricinoleic acid, has the same effect, but to a less pronounced degree.

In view of the known influence of glyceride configuration on the refractive index, it is not to be expected that the refractive indices of natural fats can be generally expressed in terms of their average molecular weight and degree of unsaturation. However, a number of equations have been proposed which are of limited application and fair accuracy. One of the best known of these is that of Pickering and Cowlishaw,[53] which is applicable to cottonseed oil, peanut, soybean oil, linseed oil, etc., and has the form:

$$n_D^{40} = 1.4515 + 0.0001171 \text{ iodine value}$$

Majors and Milner[54] found that the refractive indices of soybean oils of any one crop year can be very closely correlated with the iodine value, but that there are considerable variations from one crop year to another. However, Zeleny and co-workers[55] recommend for general use on both linseed and soybean oils the equation:

[52b] For highly unsaturated oils, such as linseed or soybean oils, the proper correction factor is more nearly 0.00036.

[53] G. F. Pickering and G. E. Cowlishaw, J. Soc. Chem. Ind., 41, 74–77 (1922).

[54] K. R. Majors and R. T. Milner, Oil & Soap, 16, 228–231 (1939).

[55] L. Zeleny and D. A. Coleman, U. S. Dept. Agr., Tech. Bull., No. 554, 1937.
L. Zeleny and M. H. Neustadt, U. S. Dept. Agr. Tech. Bull., No. 748, 1940.

$$n_{\mathrm{D}}^{25} = 1.45765 + 0.0001164 \text{ (iodine value)}$$

The above equations are applicable only to fresh oil, and not to partially oxidized or polymerized oil, which is abnormally high in refractive index. Nor are they applicable to oils which have been hydrogenated to a considerable degree.

For refractive indices of specific oils reference should be made to Chapter VI.

For data on the refractive indices of hydrogenated oils, see Chapter XVII.

The preceding values for refractive index have all referred to determinations as commonly made with light of 5890 Å. wave length, corresponding to the D line of sodium. With a mercury vapor lamp as a source of light and a suitable filter values may also be taken conveniently at 4358 Å., corresponding to the mercury G line; differences between the two, expressed in terms of dispersion, comprise a further distinguishing characteristic of fatty materials. The dispersion of saturated fatty acids and their glycerides and other esters is, unlike the refractive index, almost independent of the chain length, whereas there is a progressive increase in dispersion with the introduction of nonconjugated double bonds, and a very marked increase when the double bonds are in conjugated positions. Holmes and Pack[56] have recorded values at 25°C. of 0.0099–0.0101 for triglycerides in the series tricaprylin to tristearin, 0.0116 for olive oil, 0.0118 for cottonseed oil, 0.0131 for linseed oil, 0.0245 for oiticica oil, and 0.0274–0.0283 for American tung oil.

2. Spectral Characteristics

Pure fats and fatty acids are colorless and devoid of spectral properties in the visible range. However, all natural fats and oils contain pigments which have more or less characteristic absorption patterns. The color of fats and oils is a matter of considerable practical importance, and figures prominently in the trading rules for these materials. In the past, oils have almost invariably been graded for color by visual comparison with such standards as the Lovibond red and yellow glasses. However, this method of determining color is often unsatisfactory, being particularly inadequate in the case of oils which contain considerable amounts of green or brown pigments. The spectrophotometric method of evaluating color is widely used in controlling commercial refining and bleaching operations, and may be expected eventually to gain acceptance as a basis for trading rules.

A typical spectral absorption curve, for a sample of refined soybean oil, is reproduced in Figure 10. This curve, for an oil of greenish cast, shows the absorption maximum at about 660 mμ which is characteristic of

[56] R. L. Holmes and F. C. Pack, *J. Am. Oil Chem. Soc.*, 25, 163–167 (1948).

chlorophyll, as well as the general absorption at lower wave lengths contributed by carotenoid pigments. The curve of Figure 11, constructed with the aid of a spectrophotometer of higher resolving power than that of Figure 10, shows the absorption pattern characteristic of a specific oil—in this case, refined but unbleached cottonseed oil, with maxima at 410, 430, 455, and 480 mμ.

In anticipation of the eventual substitution of spectrophotometric color evaluation in place of matching with Lovibond color glasses for the official color grading of edible vegetable oils, the American Oil Chemists Society has recently adopted a tentative method which correlates Lovibond readings with optical densities at 460, 550, 620, and 670 mμ (Chapter XVI).
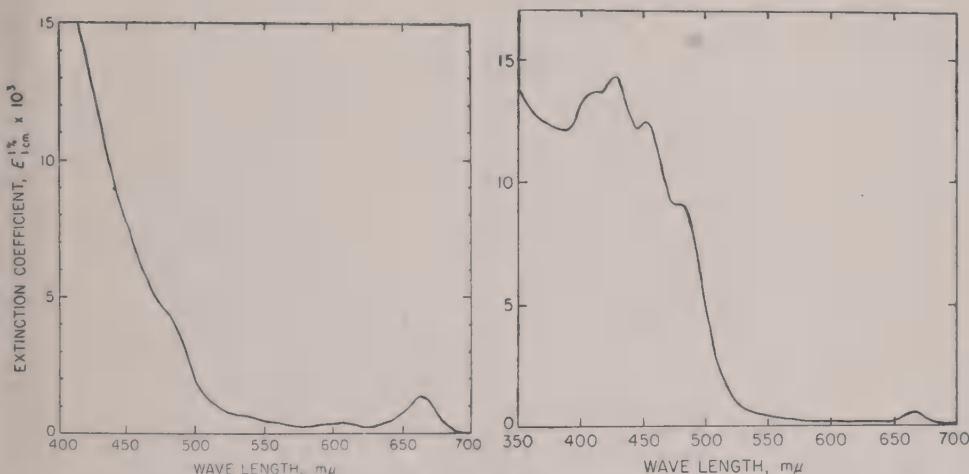
Fig. 10. Spectral absorption curve, refined soybean oil in carbon tetrachloride. Fig. 11. Spectral absorption curve, refined cottonseed oil in chloroform.

For the official color grading of relatively dark inedible tallows and greases, traders in the United States have long made use of the so-called F.A.C. color standards, consisting of aqueous solutions of various colored inorganic salts (see Chapter XVI).

Although they transmit visible light freely, pure unsaturated fatty acids and their esters absorb in the ultraviolet region. In the case of nonconjugated acids, the absorption is only of a general nature, which does not lend itself to analytical interpretation. Conjugated double bonds, however, give rise to well-defined absorption maxima which permit the quantitative determination of individual conjugated fatty acids in mixtures. A typical ultraviolet absorption curve,[57] for tung oil, a conjugated acid oil, is shown in Figure 12.

[57] R. T. O'Connor, D. C. Heinzelman, A. F. Freeman, and F. C. Pack, *Ind. Eng. Chem., Anal. Ed.*, **17**, 467–470 (1945).

Following the work of Kass, Miller, and Burr and associates,[58] a spectral technique applicable to the quantitative determination of nonconjugated acids was described by Mitchell, Kraybill, and Zscheile.[59] It involves the measurement of absorption at the proper wave lengths in
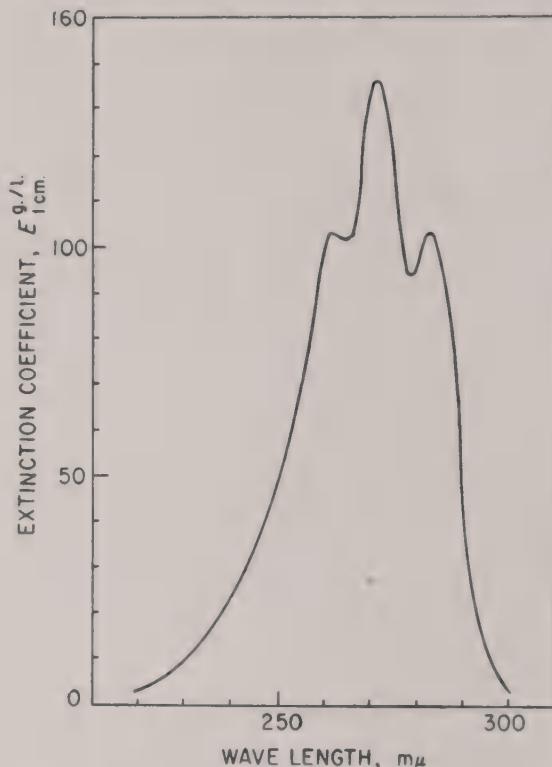
Fig. 12. Spectral absorption curve (ultraviolet), American tung oil in cyclohexane.[57]

the ultraviolet after conversion of nonconjugated acids to conjugated forms by alkali isomerization (see page 126). With minor modifications, it is now recognized as an indispensable tool of the fat analyst.

3. OPTICAL ROTATION

Optical activity is exhibited only by cyclic acids and their glycerides, such as those found in chaulmoogra oil, etc., and to a lesser extent by hydroxy acids, for example, ricinoleic acid. It is consequently a property of little interest in oil and fat technology.

[58] J. P. Kass, E. S. Miller, M. Hendrickson, and G. O. Burr, Paper presented at 99th Meeting of the American Chemical Society, April, 1940. G. O. Burr and E. S. Miller, *Chem. Revs.*, 29, 419–438 (1941).
[59] J. H. Mitchell, H. R. Kraybill, and F. P. Zscheile, *Ind. Eng. Chem.*, *Anal. Ed.*, 15, 1–3 (1943).

I. Electrical Properties

1. RESISTANCE

Dry fats and fatty acids are very poor conductors of electricity. The specific resistance of commercial stearic acid has been recorded as 0.6×10^{11} ohms at 100°C. and 22.3×10^{11} ohms at 196°C.[60] That of oleic acid has been recorded as 2×10^{11} ohms at 100°C. and 83×10^{11} ohms at 200°C.

2. DIELECTRIC CONSTANT

The dielectric constant lies in the range of about 3.0–3.2 for normal oils, and for these oils is not a particularly distinguishing characteristic. However, castor and oiticica oils, which contain substituted fatty acids (ricinoleic and licanic), have high dielectric constants. Values of 3.96 and 4.04 have been reported[61] for castor and oiticica, respectively. Values for tung oil are normal, e.g., 3.10,[61] whereas raw linseed oil is stated to be remarkably constant in the range 3.22–3.24.[62]

Oxidation increases the dielectric constant of oils through the introduction of polar groups; in the course of low-temperature air blowing, linseed oil may rise to a value of about 5.20.[62] On the other hand, heat polymerization without considerable oxidation has relatively little effect. It has recently been suggested,[62,63] therefore, that the dielectric constant is a characteristic of unique value for control of the blowing of drying oils for linoleum manufacture.

Dielectric constants of free fatty acids are not greatly different from those of the parent glycerides.

In water-in-fat emulsion products, such as butter, the dielectric constant is determined by the emulsion structure, as well as the moisture content. This characteristic is said[64] to be useful for controlling the manufacture of such products, for example, in the manufacture of butter by the new continuous process (see pages 270–271).

[60] E. L. Lederer and O. Hartleb, *Seifensieder-Ztg.*, *56*, 345–347 (1929).
[61] B. P. Caldwell and H. F. Payne, *Ind. Eng. Chem.*, *33*, 954–960 (1941).
[62] E. Hazlehurst, *Paint Industry Mag.*, *58*, No. 8, 262–270 (1943).
[63] G. A. O'Hare and W. J. Withrow, *Ind. Eng. Chem.*, *39*, 101–104 (1947).
[64] W. Mohr and C. Hennings, *Milchwissenschaft*, *2*, 173–179 (1947).

ROLE OF FATS IN DIET OF MAN

A. Fats in Human Nutrition[1]

1. INTRODUCTION

Despite the present large consumption of fats and oils in soap, paint, and other nonedible industrial products, the greater part of the world's fat production continues to be consumed as a human food.

The per capita consumption of fats in foods in the United States was estimated[2] to be 94.7 pounds in 1939. This amount was distributed among the various classes of food products as follows (in pounds):

Prepared fats, including butter	46.3
Meats and eggs	19.6
Dairy products other than butter	18.5
Nuts and cacao products	5.0
Grains and related products	2.7
Miscellaneous products	2.6
Total	*94.7*

The fat consumed was estimated to supply approximately 33% of the total per capita caloric intake.

Fats are primarily a source of energy in the diet. They are the most concentrated of all food materials, furnishing about 9 large calories of energy per gram, as compared with about 4 calories each furnished by proteins and carbohydrates. Although carbohydrates serve the same primary purpose in the diet as do fats, namely that of contributing readily available energy, they nevertheless cannot be substituted for fats to an unlimited degree. In the case of large populations shut off from normal fat supplies by the exigencies of war, it has repeatedly been observed that the ensuing restriction of the fat intake leads to a definite, mass fat hunger. This is partially explainable on the basis of the increased palatability conferred on foods by the addition of fats, and is doubtless also related to

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[1] For recent reviews on this subject, see H. J. Deuel, Jr., Chapter XIX in *Cottonseed and Cottonseed Products*, A. E. Bailey, ed., Interscience, New York, 1948; and Chapter XVIII in *Soybeans and Soybean Products*, K. S. Markley, ed., Interscience, New York, 1950.

[2] U. S. Tariff Commission, *United States Consumption of Food in Terms of Fats, Proteins, Carbohydrates, and Calories, 1939–1943*. Washington, 1944.

the manner in which fat delays the digestion of food, and thus prevents premature sensations of hunger after eating. However, it appears that there are probably other and more deep-seated reasons for the natural craving of the human organism for fatty foods.

2. Noncaloric Functions

Fats and their component fatty acids appear to perform a number of vital functions in the body which are quite unrelated to their action as energy-bearing materials.[3] Certain unsaturated fatty acids are required for the building of many kinds of body cells. As these acids apparently cannot be synthesized in the body, they must be ingested as such in food. It was demonstrated by Burr and co-workers[4] that the exclusion of fat from the diet of rats resulted in a fat-deficiency disease, characterized in the earlier stages by development of a scaly skin, in the later stages by loss of weight, kidney lesions, and finally death. The disease responded to treatment by the inclusion of either linoleic or arachidonic acids in the diet. Linolenic acid was also effective as a curative agent, although somewhat less so than the other two acids, whereas oleic acid, which is readily synthesized by the animal from carbohydrates, had no effect.

The more serious symptoms of fat deficiency have not been demonstrated in human subjects; however, lack of the above so-called "essential fatty acids" has been definitely associated with certain forms of eczema.[5]

It is significant that, of the various groups of vitamins, four—A, D, E, and K—are soluble in fat rather than in water, and hence are invariably associated with fatty foodstuffs. In addition to the fat-soluble vitamins, fats, or certain fatty acids, have been reported to perform an accessory role in the metabolism of thiamin[6] and lactose.[7]

3. Digestibility of Fats

At various times in the past, and particularly during the early days of the hydrogenation process, there has been considerable argument and discussion, largely amongst nonscientific writers, concerning the relative digestibilities of different fats. It has been demonstrated, through the

[3] For a review of the noncaloric functions of fat in the diet, see G. O. Burr and R H. Barnes, *Physiol. Revs.*, *23*, 256–278 (1943).
[4] H. M. Evans and G. O. Burr, *Proc. Soc. Exptl. Biol. Med.*, *24*, 740–743 (1926–1927). G. O. Burr and M. M. Burr, *J. Biol. Chem.*, *82*, 345–367 (1929), *86*, 587–621 (1930). G. O. Burr, M. M. Burr, and E. S. Miller, *J. Biol. Chem.*, *97*, 1–9 (1932).
[5] See, for example, W. R. Brown and A. E. Hansen, *Proc. Soc. Exptl. Biol. Med.*, *36*, 113–117 (1937).
[6] H. M. Evans and S. Lepkovsky, *Science*, *68*, 298 (1928); *J. Biol. Chem.*, *83*, 269–287 (1929); *ibid.*, *96*, 165–188 (1932). W. D. Salmon and J. G. Goodman, *J. Nutrition*, *13*, 477–500 (1937).
[7] E. J. Schantz, C. A. Elvehjem, and E. B. Hart, *J. Biol. Chem.*, *122*, 381–390 (1938). L. P. Zialciti, Jr., and H. H. Mitchell, *J. Nutrition*, *30*, 147–150 (1945). M. L. Nieft and H. J. Deuel, Jr., *J. Biol. Chem.*, *167*, 521–525 (1947).

work of Langworthy, Holmes, Deuel, and others,[8] that there are no significant differences in the digestibility of different fats and oils except in the case of those which have melting points considerably above body temperature (*ca.* 50°C. and above), and are digested somewhat less completely than lower melting products. Recent digestibility studies by Mattil and co-workers[8a] emphasize the fact that it is the melting point of the fat as a whole rather than the melting points of the component glycerides or fatty acids that determines the digestibility of any particular fat. It is to be noted that commercial hydrogenated fat products have melting points which are in general much lower than those of certain animal fats (*e.g.,* mutton fat and deer fat) which have long been accepted as wholesome products for human consumption.

4. Nutritive Values of Specific Fats

The relative nutritive values of butterfat and other edible fats have constituted the subject of much recent controversy. Recent investigations in this field have been principally concerned with the rate of growth of weanling rats on different fat diets. Superior growth on a butterfat diet has been reported by Harris and Mosher[9] and Boer.[10] On the other hand, Euler, Euler, and Säburg[11] reported butterfat to be inferior to margarine. Deuel, Movitt, Hallman, and Mattson,[12] in an extensive series of tests, could find no significant differences in a group of fats composed of butterfat, margarine, corn oil, cottonseed oil, olive oil, peanut oil, and soybean oil. In a series of investigations Schantz and Boutwell *et al.*[13] noted a specific growth-promoting property in butterfat and ascribed it to the saturated acid fraction, but subsequently reported that the superiority of butterfat was evident only when the carbohydrates in the diet consisted of lactose.

More recently, vaccenic acid (see page 13), which is present in butter, but not in vegetable oils, has been claimed to constitute a specific growth-

[8] See, for example, A. D. Holmes and H. J. Deuel, Jr., *Am. J. Physiol., 54,* 479–482 (1921); H. J. Deuel, Jr., and A. D. Holmes, *U. S. Dept. Agr. Bull.* No. 1033 (1922); C. F. Langworthy, *Ind. Eng. Chem., 15,* 276–278 (1923).
[8a] K. F. Mattil and J. W. Higgins, *J. Nutrition, 29,* 255–260 (1945). K. F. Mattil, J. W. Higgins, and H. E. Robinson, *Science, 104,* 255–256 (1946).
[9] R. S. Harris and L. M. Mosher, *Food Research, 5,* 177–184 (1940).
[10] J. Boer, *Acta Brevia Neerland, Physiol. Pharmacol. Microbiol., 11,* 180–182 (1941).
[11] B. von Euler, H. von Euler, and I. Säberg, *Arkiv Kemi Mineral. Geol., B15,* No. 8 (1941).
[12] H. J. Deuel, Jr., E. Movitt, L. F. Hallman, and F. Mattson, *J. Nutrition, 27,* 107–121 (1944).
[13] E. J. Schantz, C. A. Elvehjem, and E. B. Hart, *J. Dairy Sci., 23,* 181–189 (1940). E. J. Schantz, R. K. Boutwell, C. A. Elvehjem, and E. B. Hart, *ibid., 23,* 1205–1210 (1940). R. K. Boutwell, R. P. Geyer, C. A. Elvehjem, and E. B. Hart, *ibid., 24,* 1027–1034 (1941) and *26,* 429–437 (1943).

promoting factor.[14] However, this has been denied by other workers,[15] and subsequently it was reported by the original investigators[16] that spectroscopically pure vaccenic acid is devoid of any growth-promoting effect.

12: 13-Octadecenoic acid is likewise lacking in any unusual growth-promoting effect.[16a]

In dealing with the comparative merits of butter and margarine in the human diet, it is pertinent to consider that human milk fat and the milk fat of the cow differ greatly in composition, and that the former actually resembles a typical margarine fat more closely than it does butterfat.[17]

Nutritional aspects of the butter vs. margarine controversy have been reviewed recently by Carlson,[18] Zialciti and Mitchell,[19] and Deuel.[20]

It has been shown[21] that iso-oleic acids formed in fats by hydrogenation are nutritionally equivalent to ordinary oleic acid, and that mono- and diglycerides produce good growth in rats at reasonable levels of ingestion.[22] However, it has been shown that rats are unable to digest polymerized oils.[22a]

B. Non-nutritional Functions of Edible Fats

Edible fats have certain important non-nutritional functions. These derive principally from the distinctive physical properties of fats and oils.

Large quantities of fats are used in the production of baked goods, including bread, cakes, crackers, biscuits, cookies, and pastries. In this class of edible products the fat not only contributes to the food value, but also provides a highly essential lubricating action. Its dispersion throughout the body of the dough prevents the gluten in the flour from forming a continuous and refractory structure, and enables the product to assume its

[14] J. Boer, B. C. P. Jansen, and A. Kentie, *Nature*. *158*, 201 (1946); *J. Nutrition*, *33*, 339–360 (1947).

[15] See H. Nath, V. H. Barki. C. A. Elvehjem. and E. B. Hart, *J. Nutrition*, *36*, 761–772 (1948).

[16] J. Boer, E. H. Groot, and B. C. P. Jansen, *Voeding*, *9*, 60–62 (1948).

[16a] H. J. Deuel, Jr., S. M. Greenberg, E. E. Straub, T. Fukui, C. M. Gooding, and C. F. Brown, *J. Nutrition*, *28*, 361–368 (1949).

[17] T. P. Hilditch and M. L. Meara, *Biochem. J.*, *38*, 29 (1944). A. R. Baldwin and H. E. Longenecker, *J. Biol. Chem.*, *154*, 255 (1944).

[18] A. J. Carlson, *Science*, *99*, 413–414 (1943).

[19] L. P. Zialciti, Jr., and H. H. Mitchell, *Science*, *100*, 60–62 (1944).

[20] H. J. Deuel, Jr., *Science*, *103*, 183–187 (1946).

[21] A. D. Barbour, *J. Biol. Chem.*, *101*, 63–72 (1933).

[22] W. A. Braun and C. L. Shrewsbury, *Oil & Soap*, *18*, 249–250 (1941). S. R. Ames, M. P. O'Grady, N. D. Embree, and P. L. Harris, *J. Am. Oil Chem. Soc.*, *28*, 31–33 (1951).

[22a] S. Lassen, E. K. Bacon, and H. J. Dunn, *Arch. Biochem.*, *23*, 1–7 (1949).

characteristic form and texture during the baking operation. In addition, a plastic fat is capable of entrapping and holding considerable air in the mixing process. This air, expanding under the influence of the heat of the oven, contributes a leavening action, which is highly important in the manufacture of cakes and similar baked goods (see Chapter X).

In the frying of foods, the role of the fat is essentially that of an efficient heat transfer medium, which is especially adapted to transmitting heat rapidly and uniformly to the surface of the food being cooked. Frying has the advantage over other methods of cooking of being very rapid, and of neither drying the food excessively nor leaching its water-soluble constituents. It is now becoming generally recognized that fried foods are not necessarily less digestible than other foods of equivalent fat content, and that old prejudices against the frying of foods for children have little or no scientific justification.[23]

The contribution of fats to the flavor and palatability of foods is very important. All natural fats and oils have distinctive flavors, and the flavor of a prepared dish is often strongly influenced by the fat employed in its composition. However, the effectiveness of a fat in promoting food flavor depends to a large degree simply upon the physical properties of the fat, rather than upon any flavor of its own that the fat may carry. Perfectly neutral and tasteless oils, for example, highly deodorized cottonseed oil, are used in large quantities for "seasoning" cooked vegetables, salads, sauces, gravies, etc.

[23] F. H. Richardson, *J. Pediatrics, 24,* 199–205 (1944).

B. RAW MATERIALS FOR OIL AND FAT PRODUCTS

SOURCES, UTILIZATION, AND CLASSIFICATION OF OILS AND FATS

A. Sources of Commercial Fats

Since oils are essential constituents of all forms of plant and animal life, they are very widely distributed in nature. Every species of plant or animal develops some quantity of oil or fat during its life cycle. However, the plants and animals which produce oil in sufficient quantity and in a sufficiently available form for it to form an article of commerce are relatively few in number.

The largest source of oil at the present time consists of the seeds of annual plants, such as flax, soybean, cottonseed, peanut, etc. Some of these plants, such as the castor plant and the oil-bearing varieties of flax, are cultivated for their oil alone. Others, for example, soybeans and peanuts, produce seed which are not only a source of oil, but are also widely utilized as foods. In the case of other oil-bearing plants, such as cotton and corn, the oil is merely a by-product of a crop which is primarily grown for other purposes.

The annual oil crops are, in general, products of relatively temperate climates, and require more or less careful cultivation. They constitute a flexible portion of the world's oil and fat supplies, inasmuch as the production of any individual crop may be varied within wide limits from season to season.

A second large source of vegetable oils comprises certain oil-bearing trees, of which the coconut, oil palm, olive, and tung are the most important. The oil from the olive tree and a portion of the oil from the palm tree are derived from the pulp rather than the seed of the fruit. All the oil-bearing trees require a relatively warm climate, and two of the most important, the coconut and oil palms, are tropical trees. Both coconut and oil palms produce larger yields of oil per unit land area than do any of the annual oil crops. They also flourish in the wild state, and a large proportion of the oil produced is from stands of uncultivated or semicultivated trees.

The commercial land animal fats come almost entirely from three kinds of domestic animals—hogs, cattle, and sheep. There are other animals,

such as fowl, which are raised in large numbers, but the carcasses of these are so small that they are usually consumed without the fatty portions being separated and processed to yield a pure fat. Wild land animals are no longer a considerable source of fats except in a very few restricted regions. All three of the above-mentioned animals thrive best and are raised in the greatest numbers in temperate climates.

The production of animal body fats is approached by that of the milk fats. There are regions where the production of fat from the milk of the goat, buffalo, reindeer, etc., is of local importance, but much the greater part of the world's milk fat production consists of butterfat, derived from cow's milk. The successful husbandry of dairy cows requires not only a temperate climate, but also an intensive agriculture, with a plentiful supply of feedstuffs. Consequently, it is largely restricted to the more highly settled regions of the world, which have a high production of other agricultural products.

TABLE 28

ESTIMATED WORLD PRODUCTION OF DIFFERENT FATS AND OILS IN 1949[a]

Fat	Production, million pounds	Fat	Production, million pounds
Butterfat	6,186	Sunflowerseed oil	1,876
Lard	5,460	Sesame oil	1,386
Tallow and greases	4,440	Palm oil	1,270
Peanut oil	3,932	Palm kernel oil	920
Rapeseed oil	3,282	Whale oil	784
Cottonseed oil	3,200	Fish oils	584
Soybean oil	2,980	Castor oil	422
Coconut oil	2,600	Tung oil	270
Linseed oil	2,374	Babassu oil	84
Olive oil	1,970	*Total for principal oils*	*44,020*

[a] Office of Foreign Agricultural Relations, U. S. Dept. of Agriculture, *Foreign Agricultural Circular*, March 6, 1950.

A considerable volume of oils is contributed by the sea. Fish oils are principally derived from the more numerous, small, oily fish, such as sardines, herring, and menhaden. Most of the fish processed for oil are taken in the north Atlantic and north Pacific oceans. Fish oils, unlike animal fats, are not usually by-products of the preparation of carcasses for meat. The whole fish are processed to yield oil as the primary product, and the residue remaining after extraction of the oil is used for animal feed or as a fertilizer. The production of fish oil is surpassed by that of whale oil, which under normal conditions ranks in volume with the major vegetable oils. Whales are taken primarily for their oil, although in recent years the

recovery of by-products has assumed some importance. Most of the whale oil is produced by ships operating in the Antarctic regions.

Recent figures for the world production of most of the more important fats and oils, some of which are probably very rough estimates, are shown in Table 28.

B. Commercial Utilization of Oils and Fats

The present discussion of fat utilization will be confined to the oil and fat industry within the United States, inasmuch as complete foreign statistical data are not available, and, in any case, conditions abroad are at the present writing (1950) far from normal. Mention may be made, however, of certain long-standing differences in the utilization of fats as food materials, here and abroad. The vegetable shortening industry, which furnishes a considerable proportion of the edible fat consumed in the United States, is relatively unimportant in almost all other countries, and in some is, in fact, nonexistent. In the same proportion, the consumption of certain other edible fats is normally greater abroad, with margarine being the most popular product in the northern European countries, and olive oil and other liquid oils being preferred in the Mediterranean region. Cottonseed and soybean oils, the predominant North American edible vegetable oils, by no means dominate the foreign edible field. Peanut oil is a much more important commodity in Europe than in the United States, and palm, palm kernel, rapeseed, and whale oils, which find little or no use in this country in food products, are major oils in Europe. In eastern Europe and the Orient, rapeseed, sesame, and sunflowerseed oils are important edible oils. In South America, a major factor in edible oils is the large Argentine production of sunflowerseed oil.

The vegetable oil supplies of western Europe are normally derived in large part from oil seeds imported from Africa, India, China, Manchuria, and the East Indies and other islands of the South Pacific. In the past, Australia, New Zealand, Denmark, and the Netherlands have been exporters of butter to the United Kingdom and Germany. International trade in lard has always been large, consisting for the most part of exports from the United States to the United Kingdom and Germany. South America, Australia, and New Zealand are large exporters of tallows. South America is also the source of large quantities of exported vegetable oils or oil seeds, with Brazil being the largest producer of castor beans (and the only producer of babassu and oiticica oils) and Argentina the largest producer of flaxseed and sunflowerseed. Almost the entire world production of tung oil is from China. Except with respect to coconut and tung oils, and to some degree, linseed oil, the United States is largely self-sufficient in oil and fat supplies, but elsewhere (outside of Russia) in-

dustry is highly dependent upon a heavy flow of fats and oils or oil seeds from the less industrialized regions of the globe to those where industry and manufacturing are more highly developed.

The consumption of fats and oils in edible products in the United States in representative years during the last two decades is shown in Table 29A. A reduced per capita consumption of 2–3 pounds in recent

TABLE 29A

CIVILIAN CONSUMPTION OF FATS AND OILS IN EDIBLE PRODUCTS IN THE UNITED STATES[a]

Fat	1949		1939		1929	
	Total, million pounds	Pounds per capita	Total, million pounds	Pounds per capita	Total, million pounds	Pounds per capita
Butter[b]	1276	8.5	1830	13.9	1620	14.0
Margarine[b]	695	4.6	243	1.8	303	2.5
Both products	1971	13.1	2073	15.7	1923	16.5
Lard	1776	11.8	1662	12.6	1549	12.7
Shortening	1443	9.6	1396	10.6	1220	9.9
Both products	3219	21.4	3058	23.2	2769	22.6
Edible oils	1286	8.6	946	7.2	647	5.4
Total	6476	43.1	6077	46.1	5339	44.5

[a] *Agricultural Statistics, 1948*, U. S. Dept. Agr.; *The Fats and Oils Situation*, Bureau of Agricultural Economics, U. S. Dept. Agr., July–Aug. 1950.
[b] Basis actual fat content (assumed to be 80.5% of product weight), rather than product weight.

TABLE 29B

CIVILIAN CONSUMPTION OF FATS AND OILS IN NONEDIBLE PRODUCTS IN THE UNITED STATES[a]

Fat	1947		1939		1931	
	Total, million pounds	Pounds per capita	Total, million pounds	Pounds per capita	Total, million pounds	Pounds per capita
Soap	2143	14.9	1741	13.2	1498	12.0
Drying oil products	972	6.8	825	6.3	621	5.0
Other industrial products	824	5.7	483	3.7	314	2.5
Total	3939	27.4	3049	23.2	2433	19.5

[a] *Agricultural Statistics, 1949*, U. S. Dept. Agr.

years is accounted for by a greatly decreased production and consumption of butter, which has not been compensated by an increased consumption of margarine. Lard and shortening, like butter and margarine, are used for more or less the same purposes, and the combined per capita consumption of the two has not changed significantly for some time. Normally, shortening consumption goes up when lard consumption goes down, and *vice versa*. The per capita consumption of liquid oils (much of which

goes into mayonnaise and salad dressing) advanced steadily up to about 1938, but now appears to have leveled off to some extent.

Similar data on the consumption of fats for industrial or nonedible purposes are given in Table 29B. Although the statistics up to and including 1947 show a more or less steadily increasing consumption of fats for industrial use, it may be mentioned that preliminary figures for 1948 and 1949 indicate a decline, which may be attributed, at least in part, to the increasing manufacture of detergents from nonfatty materials.

TABLE 30

TOTAL APPARENT DOMESTIC DISAPPEARANCE OF FATS AND OILS OTHER THAN BUTTER-
FAT (CRUDE OIL BASIS) IN THE UNITED STATES IN 1948[a]

Oil	1000 lbs.	Oil	1000 lbs.
Babassu	39,041	Olive oil, edible	37,488
Castor	128,396	Olive oil, inedible and foots	2,426
Coconut	666,626	Palm	51,248
Corn	194,057	Peanut	132,189
Cottonseed	1,367,959	Perilla	15
Fish and fish liver	116,126	Rapeseed	6,273
Lard and rendered pork fat	2,033,436	Sesame	12,113
Linseed	600,452	Soybean	1,470,464
Marine mammal	15,608	Tallow, edible	65,583
Neatsfoot	2,176	Tallow, inedible and greases	1,783,972
Oiticica	13,115	Tung	129,739
Oleo oil	38,010	Wool grease	21,579
Oleostearine and oleo stock	26,465	Other vegetable oils	28,637
		Total	*8,983,193*

[a] *Agricultural Statistics*, 1949, U. S. Dept. Agr. Figures for inedible olive oil and olive oil foots, perilla oil, and rapeseed oil are for factory consumption, rather than total disappearance.

The total consumption of the more important individual fats and oils in the United States in 1948 is shown in Table 30. It is to be noted that the total does not include approximately 1,210,000 thousand pounds of butterfat. With respect to corn, cottonseed, fish, linseed, neatsfoot, peanut, and soybean oils, and lard, tallow, and greases and their derived products, the figures may be taken as representing approximately the United States' production. In some years (but not in 1948) considerable linseed oil or its oil seed equivalent is imported. The United States' production of tung oil and of olive oil does not exceed about 10–12 million pounds and 4–5 million pounds, respectively, yearly, and babassu, castor, coconut, oiticica, palm, rapeseed, and sesame oils are wholly imported.

Average wholesale prices of certain fats and oils during the month of November, 1950, are shown in Table 31.

TABLE 31

AVERAGE WHOLESALE PRICES OF FATS AND OILS DURING NOVEMBER, 1950[a]

Fat or oil	Price, cents per pound
Babassu oil, tanks, New York	20.8
Butter, 92-score, Chicago	64.0
Coconut oil, Manila, crude, tanks, Pacific Coast[b]	20.1
Corn oil, crude, tanks, midwestern mills	20.6
Cottonseed oil, crude, tanks, southeastern mills	20.6
Castor oil, No. 3, drums, New York	25.0
Cod oil, Newfoundland, drums, New York	12.5
Cod-liver oil, med. u.s.p., bbls., New York	23.4
Degras, common, bbls., New York	11.5
Grease, A White, Chicago	12.6
Grease, Yellow, Chicago	10.9
Lard, loose, Chicago	13.7
Lard, P.S., tierces, Chicago	13.9
Linseed oil, raw, tanks, Minneapolis	15.4
Menhaden oil, light pressed, tanks, New York	15.2
Neatsfoot oil, 30°, drums, New York	31.2
Oiticia oil, drums, New York	21.5
Oleo oil, extra, drums, Chicago	16.8
Oleostearine, bbls., New York	17.0
Olive oil, imported, edible, drums, New York	38.5
Olive oil foots, domestic, drums, New York	17.4
Palm oil, Congo, drums, New York[b]	21.2
Peanut oil, crude, tanks, southeastern mills	22.2
Rapeseed oil, refined, dentured, tanks, New York	23.0
Sardine oil, crude, tanks, Pacific Coast	12.6
Sesame oil, refined, drums, New York	31.5
Soybean oil, crude, tanks, midwestern mills	17.1
Tallow, inedible, Prime or Extra, Chicago	13.4
Tallow, inedible, No. 1, Chicago	11.4
Tung oil, domestic, tanks, mills	24.8

[a] *The Fats and Oils Situation*, Bureau of Agricultural Economics, U. S. Dept. Agr., November, 1950.
[b] Includes three cents per pound processing tax.

C. Classification of Fats and Oils

It is customary to classify the various fats and oils on the basis of their iodine values, into nondrying, semidrying, and drying oils. However, this system of classification fails to take into account a number of important distinctions within the three broad classes. From the standpoint of their industrial utilization they are more rationally divided into the following groups.

1. MILK FAT GROUP

The fats of this group are derived entirely from the milk of domesticated land animals. All of the various members of the group are very

similar in composition. The principal acids in the milk fats are not different from those in many other fats, consisting of oleic, palmitic, and stearic acids. These fats are distinguished from others, however, by subordinate contents of a very wide assortment of low molecular weight acids, which range downward in number of carbon atoms to butyric acid. They are the only fats which contain butyric acid in appreciable quantities. In addition to the lower molecular weight saturated acids, the milk fats also contain small amounts of monoethenoid acids with 10, 12, 14, and 16 carbon atoms, as well as traces of highly unsaturated acids of the arachidonic type. These fats are utilized wholly for edible purposes, being barred from other uses by their expensiveness in comparison with other fats.

2. Lauric Acid Group

The fats of this group are all derived from the seeds of species of palms, such as the coconut, oil palm, babassu, etc. They are distinguished from other fats by their high content of lauric acid (40–50%). They contain smaller amounts of saturated acids with 8, 10, 14, 16, and 18 carbon atoms. Their unsaturated acids are minor in amount and consist of oleic and linoleic acids; they are the least unsaturated of all the fats. Because of the low molecular weight of their acids, these fats possess the distinctive combination of a very low degree of unsaturation and a relatively low melting point. For this reason they are valuable edible fats for certain purposes. Their sodium soaps are hard and stable toward oxidation, but also freely soluble, hence they are particularly prized for soapmaking. They are also the sole source of low molecular weight fatty acids for the preparation of certain important fatty acid derivatives. Because of their tropical origin, and the fact that the plants are perennial in growth and do not require intensive cultivation, they are relatively plentiful and cheap.

3. Vegetable Butter Group

The vegetable butters are obtained from the seeds of various tropical trees. They are somewhat similar to the lauric acid oils in their property of softening and melting over a narrow temperature range. Their distinctive consistency is not due to the presence of low molecular weight acids, however, but rather to the particular configuration of their glycerides. Although they all contain 50% or more of saturated C_{14} to C_{18} acids, these acids are grouped with the unsaturated acids (oleic and linoleic) in the glycerides in such a manner as to avoid almost wholly the presence of trisaturated glycerides. The representative fat of this group is cocoa butter. The vegetable butters are relatively high-priced fats and are used chiefly in the manufacture of confections and pharmaceutical products.

4. Animal Fat Group

This group consists of the body fats of domestic land animals (lard, tallow, etc.). These fats are characterized by a high content of C_{16} and C_{18} fatty acids and a comparatively low degree of unsaturation. Their unsaturated acids consist almost entirely of oleic and linoleic acids. Although similar to the vegetable butters in fatty acid composition, they are quite different with respect to the configuration of their glycerides. They contain considerable proportions of fully saturated glycerides, which give them an extended plastic range. They are important edible fats; such portions of the production as are suitable are generally used for this purpose. However, because they are in some cases derived from animals or parts of carcasses which are unfit for consumption as food, a considerable part of the total production appears on the market as inedible fats. These are principally used in the manufacture of soap, of which they may be considered the basic ingredient.

The animal fats are generally priced somewhat below most of the vegetable oils.

5. Oleic-Linoleic Acid Group

This is the largest of the various groups and the one within which there is the most variation in the composition and characteristics of the individual oils. The oils of this group are all of vegetable origin. They consist predominantly of unsaturated fatty acids; in most cases the saturated acids comprise less than 20% of the total. Their unsaturated acids consist of oleic and linoleic acids. Linolenic acid or other acids more unsaturated than linoleic are wholly absent.

As is the case with other vegetable oils, the fatty acids of the oleic-linoleic acid oils are so distributed as to form negligible proportions of trisaturated glycerides. Consequently, most members of the group are liquid except at quite low temperatures. Most of the oils, for example, cottonseed and peanut oils, are derived from the seeds of annual plants. Olive and palm oils, however, are obtained from tree fruits, and kapok oil is expressed from the seed of a tree. Most of the plants producing oils of this group grow best in a relatively warm climate.

The oleic-linoleic acid oils are the most widely useful and the most adaptable of all the fats and oils. They are not sufficiently unsaturated to have more than weakly drying properties, so they are not used to any extent in paints or other protective coatings. However, they are excellent edible oils. Since they contain no linolenic or other highly unsaturated acids, they are free from any serious tendency toward flavor reversion. Although normally liquid, they may be converted by hydro-

genation to plastic fats of any desired degree of hardness. Thus, the same oil may serve equally well for the manufacture of either liquid or plastic edible fats. Palm oil produces firm, stable soaps of desirable properties. Most of the other oils of the group are too much sought after as edible fats to find much use in soapmaking, and in addition are too unsaturated to yield soaps of a desirable degree of hardness and stability. They may be hydrogenated, however, to form suitable hard soap fats, and a certain amount of these oils is regularly used in the preparation of soft soaps and in blends with harder fats.

The oleic-linoleic acid oils may in general be considered medium priced fats, somewhat more expensive than most other vegetable oils or the less choice animal fats, but much less expensive than butterfat.

The more important members of the oleic-linoleic acid group include cottonseed, peanut, sesame, corn, sunflower, olive, and palm oils.

6. ERUCIC ACID GROUP

The members of this group, of which only mustard, ravison, and rapeseed oil are commercially important, are distinguished by a high content of erucic acid. They also contain a small amount of linolenic acid. These oils are produced principally in certain Far Eastern countries, and in Continental Europe, where they are used for edible and other purposes. In the United States they are principally utilized in nonedible fields, for example, in the manufacture of lubricants.

In comparison with most other vegetable oils, these oils are normally cheap.

7. LINOLENIC ACID GROUP

The oils of this group are distinguished by containing some amount of linolenic acid, in addition to oleic and linoleic acids. The most important members of the group are derived from the seeds of annual plants. Unlike most of the oil-bearing plants discussed previously, the plants which produce these oils thrive best in a relatively cool climate.

The linolenic acid oils all have drying properties, hence are used in paints and similar products. Due to their tendency to revert in flavor with slight oxidation, these oils are not considered as desirable for edible purposes as the oleic-linoleic acid oils, although in the case of soybean oil most of the oil produced is used in food products. They are used relatively little for soapmaking, for reasons similar to those which limit the use of the oleic-linoleic acid oils for the same purpose. They are usually somewhat cheaper than most of the oleic-linoleic acid oils.

The most important members of the group are linseed, perilla, soybean, and hempseed oils.

8. CONJUGATED ACID GROUP

The oils of this group are differentiated from others by containing fatty acids with conjugated double bonds. The commercially important members of the group are tung oil, which consists largely of elaeostearic acid, and oiticica oil, which consists largely of licanic acid. Both of these oils are derived from the seeds of trees requiring a mild climate.

Because of the conjugate position of the double bonds in their fatty acids, which favors oxidation and polymerization, these oils dry more strongly and rapidly than ordinary drying oils. Consequently, they are in much demand for the manufacture of certain varieties of varnishes, enamels, and other protective coatings. They are unsuitable for either edible purposes or soapmaking. Since China is the single large source of an oil of this type, the price of the conjugated acid oils is largely dependent upon the availability of the Chinese crop of tung oil.

9. MARINE OIL GROUP

These oils are distinguished by the diversity of their unsaturated fatty acids. They contain large proportions of C_{16}, C_{20}, and C_{22} unsaturated acids in addition to the C_{18} acids which are common in other fats, and some of their C_{20} and C_{22} acids contain more than three double bonds. The group comprises both fish oils and marine mammal oils, such as whale oil.

As a class, the marine oils are among the cheapest of all fats and oils. They are used in edible fat products, in soap, and in protective coatings, although in none of these fields are they considered as desirable raw materials as ordinary vegetable and animal fats.

Fish liver oils constitute a special class of oils which are highly valuable as a source of vitamins A and D, and are but little used for ordinary edible or industrial purposes.

10. HYDROXY ACID GROUP

The sole representative of this group is castor oil, which is unique in consisting largely of glycerides of ricinoleic or hydroxyoleic acid. Due to its high content of this unusual acid, castor oil is different in many respects from any other oil. It is not edible and not used to any extent in soapmaking. By the dehydration process it can be converted to a conjugated acid oil somewhat similar to tung or oticica oil; hence it is extensively used in the protective coating industry. It also has many specialty uses, as a lubricant, as an oil for sulfonation, as a fluid for hydraulic systems, etc.

COMPOSITION AND CHARACTERISTICS OF INDIVIDUAL FATS AND OILS[1]

A. Introduction

In the following pages are selected analytical data on all the fats and oils of any considerable industrial importance, including a few whose importance is potential rather than actual. The special characteristics which are particularly indicative of oil quality and value, and which form the basis of trading rules, are not treated here in any systematic way, inasmuch as they will be covered fully in Chapter XIV.

The significance and reliability of reported data on the composition of the different classes of oils require some comment. With respect to the milk fats, lauric acid oils, vegetable butters, animal fats, oleic-linoleic acid oils, and hydroxy acid oils, it may be said that the older analyses are, in general, reasonably accurate. The more careful modern work on these oils has in many cases detected the presence of minor fatty acids over-looked by older analysts, but has not contributed anything new with respect to the proportions of the major acids. It is still customary and perfectly satisfactory in routine analysis of, for example, the oleic-linoleic acid oils to report the contents of "saturated," "oleic," and "linoleic" acids, and to partition the "saturated" acids between palmitic and stearic, without regard for the fact that the saturated fraction usually contains appreciable amounts of other acids in the saturated series, and that the unsaturated acids are not composed entirely of C_{18} members. In particular, it is now known that a considerable proportion of the "oleic" or dienoic acids of animal fats consists of C_{16} or lower acids, but this does not appear to bear on the practical utilization of the fats in any very important way.

A somewhat different situation exists with respect to the oils containing linolenic acid (including the erucic acid oils), the conjugated acid oils, and the marine oils. In the linolenic acid group, distribution of acids in

[1] GENERAL REFERENCES: (a) T. P. Hilditch, *The Chemical Constitution of Natural Fats*, 2nd ed., Chapman and Hall, London, 1947; (b) G. S. Jamieson, *Vegetable Fats and Oils*, 2nd ed., Reinhold, New York 1943; (c) J. A. Lovern, *The Composition of the Depot Fats of Aquatic Animals*, Food Investigation Special Report No. 51, H. M. Stationery Office, London, 1942; (d) K. A. Williams, *Oils, Fats, and Fatty Foods— Their Practical Examination*, Blakiston, Philadelphia, 1950.

the unsaturated fraction among oleic, linoleic, and linolenic acids was formerly made upon the basis of yields of insoluble bromide derivatives (of linolenic acid), and later upon the basis of a theoretical thiocyanogen absorption for the three acids. Only since about 1939 has it been generally recognized that the yields of bromides are variable and unpredictable, and that the absorption of thiocyanogen by linoleic and linolenic acids is substantially less than was first assumed. Hence, analyses published before this date may be regarded with suspicion. The effect of using theoretical rather than empirical thiocyanogen values for estimation of the fatty acid composition is to make the calculated linoleic acid content much too high and the oleic and linolenic acid contents correspondingly low. In some cases it is possible to improve the older estimates by recalculation. The recently developed alkali isomerization–spectral technique for polyethenoid acids promises to be an even better method for the linolenic acid oils. However, it needs further study and development, particularly with respect to its use in detecting and estimating very small amounts of specific acids. Some of the early workers who used this method reported the presence of small proportions of linolenic acid in a great many vegetable oils previously believed to contain no acid more unsaturated than linoleic. Since subsequent investigation revealed that the assumed linolenic acid gave no bromine addition products when concentrated by fractional crystallization of the oil, and that it actually increased during the course of catalytic hydrogenation, a mistaken interpretation of the spectral results was obvious.

The spectral method gives better estimates of elaeostearic acid or other conjugated acids than previously used chemical methods, and is even able to distinguish between the liquid and solid "alpha" and "beta" isomers of elaeostearic acid.

The marine oils present a particularly difficult problem in the determination of fatty acid composition, because the more highly unsaturated acids can be satisfactorily sorted according to chain length only by fractional distillation, and even with every precaution, they are much inclined to polymerize and otherwise undergo heat alteration during the process. Even the best modern analyses only approximate the proportions and the average degree of unsaturation of the more unsaturated members of higher chain length.

B. Milk Fats

1. Butterfat (from Cow Milk)

Butterfat is distinguished by an extraordinary variety of component fatty acids. Every member of the saturated acid series from butyric (C_4)

to behenic (C_{22}) is present, with the possible exception of arachidic (C_{20})[2]; and each member of the monoethenoid series from decenoic to octadece-

TABLE 32

COMPOSITION (PER CENT BY WEIGHT) AND CERTAIN CHARACTERISTICS OF BUTTERFAT OF DIFFERENT IODINE VALUES

Analysis	Jack and co-workers[a]	Hilditch and Jasperson[b]	Hilditch and Jasperson[b]
Characteristics			
Iodine value...............	32.9	37.5	42.9
Saponification equiv.........	236.3	247.7	251.8
Reichert-Meissl value........	32.5	26.1	27.4
Polenske value....	—	1.85	1.78
Kirschner value.............	—	21.8	21.8
Composition of fatty acids			
Butyric...................	3.5	3.6	3.7
Caproic...................	1.4	2.0	1.7
Caprylic..................	1.7	0.5	1.0
Capric....................	2.6	2.3	1.9
Lauric....................	4.5	2.5	2.8
Myristic..................	14.6	11.1	8.1
Palmitic..................	30.2	29.0	25.9
Stearic...................	10.5	9.2	11.2
Above C_{18}.................	1.6	2.4	1.2
Total saturated.............	*70.6*	*62.6*	*57.5*
Decenoic.................	0.3	0.1	0.1
Dodecenoic...............	0.2	0.1	0.2
Tetradecenoic.............	1.5	0.9	0.6
Hexadecenoic.............	5.7	4.6	3.4
Octadecenoic (oleic, etc.).....	18.7	26.7	32.8
Octadecadienoic...........	2.1	3.6	3.7
C_{20} and C_{22} unsat......	0.9	1.4	1.7
Total unsaturated...........	*29.4*	*37.4*	*42.5*

[a] J. L. Henderson and E. L. Jack, *Oil & Soap*, *21*, 90–92 (1944). E. L. Jack and J. L. Henderson, *J. Dairy Sci.*, *28*, 65–78 (1945). E. L. Jack, J. L. Henderson, and E. B. Hinshaw, *J. Biol. Chem.*, *162*, 119–128 (1946).
[b] T. P. Hilditch and H. Jasperson, *J. Soc. Chem. Ind.*, *60*, 305–310 (1941).

noic. An octadecadienoic acid is present in appreciable amounts, as well as traces of octadecatrienoic acid[3] and highly unsaturated C_{20} and C_{22} acids, including arachidonic.[2,4]

Traces of dihydroxystearic acid have been detected,[5] and also of a hydroxy palmitic acid.[6]   A very small proportion of the octadecenoic acid

[2] A. W. Bosworth and E. W. Sisson, *J. Biol. Chem.*, *107*, 489–496 (1934).
[3] T. P. Hilditch and H. Jasperson, *J. Soc. Chem. Ind.*, *64*, 109–111 (1945).
[4] A. W. Bosworth and J. B. Brown, *J. Biol. Chem.*, *103*, 115–134 (1933).
[5] C. A. Browne, *J. Am. Chem. Soc.*, *21*, 807–827 (1899).
[6] A. W. Bosworth and G. E. Helz, *J. Biol. Chem.*, *112*, 489–492 (1936).

consists, not of oleic acid, but of the 11:12 *trans*-isomer, vaccenic acid.[7] The octadecadienoic acid apparently is not normal linoleic acid, but probably either the 9:10 *cis*-, 12:13 *trans*- or the 9:10 *trans*-, 12:13 *cis*-isomer.[3] In the older analyses, all monoethenoid and all polyethenoid acids are commonly grouped as oleic and linoleic acids, respectively.

Representative analyses of butterfat of varying iodine value—in terms of component fatty acids—are given in Table 32. For information on the glyceride composition of butterfat, reference should be made to Hilditch.[1a]

There is a rather pronounced seasonal change in the fatty acid composition of butterfat, which is normally several iodine value units higher in the summer than in the winter, with corresponding variation in the relative proportions of unsaturated and saturated fatty acids. The change is associated with differences in the feed of the animals at the different seasons, but perhaps not altogether so, since cows put on green pasturage produce softer butterfat even if their feed has previously consisted of hay or ensilage comparable in solid composition to the green feed. An effect of temperature, or of increased activity of the animals has been suggested.[1a] There are also differences in the butterfat of different cows on identical rations, and the age of the animal has some influence upon butterfat composition as also has the duration of the period of lactation.

The ingestion of mono-, di-, or triethenoid acids or of saturated acids of high or low molecular weight in the feed appears to have little effect upon the butterfat, but the saturated acids of medium molecular weight, including lauric, myristic, and palmitic, appear to be able to pass directly into the milk fat.[8] Consequently, the feeding of oil cakes containing these acids, *i.e.*, coconut, palm kernel, or cottonseed cakes, increases the content of saturated acids and produces a relatively hard butter. American butter appears to be generally firmer and lower in iodine value than European butters. The effect of different rations on the composition and characteristics of butterfat will be discussed at greater length in a subsequent chapter on butter and margarine.

Butterfat is distinguished from other oils except those of the lauric acid group by the low average molecular weight of its fatty acids (manifested in a high saponification value and a low refractive index), and from coconut oil and other lauric acid oils by its high content of steam-volatile acids, as indicated by a high Reichert-Meissl value. The distinctive characteristics of butterfat, in comparison with lauric acid oils and other oils, are summarized in Table 33. Elsdon and Smith[8a] and, more recently Will-

[7] R. P. Geyer, H. Nath, V. H. Barki, C. A. Elvehjem, and E. B. Hart, *J. Biol. Chem.*, *169*, 227–228 (1947).

[8] T. P. Hilditch and J. J. Sleightholme, *Biochem. J.*, *24*, 1098–1113 (1930); *25*, 507–522 (1931).

[8a] G. D. Elsdon and P. Smith, *Analyst*, *52*, 63–66 (1927); *Oil & Fat Ind.*, *4*, 103–105, 111 (1927).

TABLE 33

DISTINCTIVE CHARACTERISTICS OF BUTTERFAT IN COMPARISON WITH
OTHER FATS AND OILS

Analysis	Butterfat	Coconut oil	Palm kernel oil	Ordinary fats and oils
Saponification value..........	210–240	245–260	240–250	Below 200
Refractive index at 60°C......	*ca.* 1.4465	*ca.* 1.4410	*ca.* 1.4430	Over 1.4465[a]
Reichert-Meissl value.........	22–34	6–8	5–7	<1
Polenske...................	2–4	14–18	10–12	<1
Kirschner value.............	20–26	1–2	0.5–1	<0.5

[a] Unless the iodine value is very nearly zero.

iams,[9] have published extensive data on the Reichert-Meissl, Polenske, and Kirschner values of mixtures of butterfat, coconut, and palm kernel oils. In addition to the characteristics mentioned above, other average characteristics of butterfat are approximately as follows: density at 60°C., 0.887; melting point, 38°C.; titer, 34°C.; unsaponifiable matter, 0.4%.

From the standpoint of the nutritional value of the product, the vitamin A content of butter is important. Since the source of the vitamin A in butter is the β-carotene or other carotenoid pigments in the feed of the cows, the content of this vitamin varies considerably, being highest in the summer when the dairy herds are on pasture, and lowest in the winter when there are no green feedstuffs in their rations. A portion of the carotene in the feed is transferred to the butterfat without change. The amount of carotene ingested by the cow into the butterfat exhibits a variation with the feeding regime parallel to variations in the production of vitamin A, so that the depth of yellow color in the butter serves to some extent to indicate its vitamin A content.

Actually, the entire vitamin A potency of butter is in part due to vitamin A as such, and in part due to carotene, which is partially converted to the vitamin in the human body. The average relative biological activities of vitamin A and carotene can hardly be regarded as settled. One International Unit of vitamin A is defined as the amount possessing the biological activity of 0.6 μg. of pure β-carotene.[9a] The biological activity of pure vitamin A was for some time considered to be about 3,000,000 I.U. per gram. However, recent work[10] has indicated that the activity of this vitamin, either as such or in the form of its esters, is in the neighborhood of 4,000,000 I.U. per gram. On this basis the vitamin A potency of butter would be expressed by the following equation:

[9] K. A. Williams, *Analyst*, *74*, 504–510 (1949).
[9a] Although International units and U.S.P. units are ordinarily taken as equivalent, this is not strictly justified (see page 37).
[10] J. G. Baxter and C. D. Robeson, *J. Am. Chem. Soc.*, *64*, 2411–2416 (1942). K. Hickman, *Ann. Rev. Biochem.*, *12*, 353–396 (1943).

$$I.U. = 4.0\,S + 1.67\,C$$

where I.U. = International Units per gram; S = vitamin A content in μg. per gram; and C = carotene content in μg. per gram.

Recently, very comprehensive information on the vitamin A potency of butter in the United States has been made available through a nation-wide survey, covering all seasons of the year, sponsored by the United States Department of Agriculture.[11] Computed upon the basis outlined above, the average winter potency throughout the country was 11,160 I.U.

TABLE 34

CAROTENE AND VITAMIN A CONTENTS OF BUTTERFAT FROM DIFFERENT BREEDS OF COWS ON SUMMER AND WINTER RATIONS

(Content in μg. per g. dry fat)

Season and breed	Baumann, Steenbock, Beeson, and Rupel[a]		Gillam, Heilbron, Ferguson, and Watson[b]		Booth, Kon, and Gillam[c]	
	Carotene	Vitamin A	Carotene	Vitamin A	Carotene	Vitamin A
SUMMER						
Ayrshire	5.5	12.2	4.1	11.8	—	—
Brown Swiss	9.8	13.8	—	—	—	—
Friesian	—	—	4.7	12.1	—	—
Guernsey	17.0	18.5	11.4	9.5	22.4	8.9
Holstein	6.6	15.1	—	—	—	—
Jersey	10.7	11.5	—	—	—	—
Shorthorn	—	—	2.9	8.4	7.8	11.0
WINTER						
Ayrshire	4.8	8.4	2.7	6.6	—	—
Brown Swiss	6.0	7.8	—	—	—	—
Friesian	—	—	3.5	6.1	—	—
Guernsey	10.3	6.8	7.3	5.4	5.0	3.4
Holstein	5.2	10.2	—	—	—	—
Jersey	7.1	7.1	—	—	—	—
Shorthorn	—	—	2.5	5.8	1.9	3.9

[a] C. A. Baumann, H. Steenbock, W. M. Beeson, and I. W. Rupel, *J. Biol. Chem.*, *105*, 167–176 (1934).

[b] A. E. Gillam, I. M. Heilbron, W. S. Ferguson, and S. J. Watson, *Biochem. J.*, *30*, 1728–1734 (1936).

[c] R. G. Booth, S. K. Kon, and A. E. Gillam, *Biochem. J.*, *28*, 2169–2174 (1934).

per pound, and the average summer potency was 17,955 I.U. per pound. The results of Jenness and Palmer[12] on 1019 samples of Minnesota butter may be considered more or less typical of those for the individual states. In the period of lowest potency, January 1 to April 22, the average vita-

[11] L. A. Maynard, C. A. Cary, C. J. Koehn, W. D. Salmon, H. R. Guilbert, F. P. Zscheile, G. W. Snedecor, L. S. Palmer, W. F. Gesses, I. L. Hathaway, and W. H. Peterson, *U. S. Dept. Agr. Misc. Pub.*, *571* (1945). See also various reports on the individual state-wide surveys, appearing during the period 1943–1946, in *J. Dairy Sci.* and *J. Nutrition.*

[12] R. Jenness and L. S. Palmer, *J. Dairy Sci.*, *28*, 473–494 (1945).

min A potency was 9000–10,000 I.U. per pound; in the period of greatest potency, May 21 to early October, it was 16,500 to 18,500. Of the entire lot of samples, 90% had a vitamin A potency over 9000, and 45% over 15,000. In the summer butter, 21–25% of the total vitamin A potency was contributed by carotene, and 75–79% by vitamin A as such. In winter butter, the relative proportions were 11–15% and 85–89%, respectively.

The vitamin A content of butter is thus usually within the range of about 6–12 μg. per gram and the carotene content in the range 2–10 μg. per gram. The distribution of vitamin A and carotene is a breed characteristic. Shorthorn cows produce relatively pale butters which are low in carotene content, but not correspondingly low in vitamin A. Guernsey cows produce butterfat which is high in carotene and strongly colored, but not particularly high in content of vitamin A. Holstein cows have been found to be outstanding in the high vitamin A content of their butterfat, particularly in the winter.

Carotene and vitamin A contents of butterfat from winter and summer butters of different breeds of cows, as reported by two different groups of observers, are listed in Table 34. In this table, the results of Baumann et al.[13] represent tests made on American butters, while those of Gillam et al.[14] and Booth et al.[15] are from the examination of English butters. The somewhat higher values for vitamin A reported by the former group may be attributed in part to the use of a different method of calculating contents of this vitamin from spectrophotometric data, and probably do not represent real differences in the two varieties of butter. In either case, the results are not necessarily the same as would be obtained by the methods used by more recent workers.

The vitamin A potency of butterfat may be increased, even to very high levels, e.g., 175,000 I.U. per pound, by the feeding of vitamin A concentrates to the milk cows.[16] Except when concentrates are fed, vitamin A in the butterfat is derived purely from carotene in the feed.

The vitamin D content of butter is much less significant than that of vitamin A, but is nevertheless appreciable. It varies from about 0.1 to 1.0 I.U. per gram, being highest in the summer, and lowest in the winter.

2. Other Milk Fats

The milk fat of other grazing animals is generally similar, in composition and characteristics, to the milk fat of cows. Analyses of milk fats

[13] C. A. Baumann, H. Steenbock, W. M. Beeson, and I. W. Rupel, J. Biol. Chem., 105, 167–176 (1934).
[14] A. E. Gillam, I. M. Heilbron, W. S. Ferguson, and S. J. Watson, Biochem. J., 30, 1728–1734 (1936).
[15] R. G. Booth, S. K. Kon, and A. E. Gillam, Biochem. J., 28, 2169–2174 (1934).
[16] H. J. Deuel, Jr., N. Halliday, L. F. Hallman, C. Johnston, and A. J. Miller, J. Nutrition, 22, 303–313 (1941). K. L. Blaxter, S. K. Kon, and S. Y. Thompson, J. Dairy Research, 14, 225–230 (1946).

from various animals other than the cow are contained in Table 35. In connection with miscellaneous milk fats it may be mentioned that Indian ghee may legally be composed of fat derived from the milk of cows,

TABLE 35

COMPOSITION (PER CENT BY WEIGHT) AND CHARACTERISTICS OF
MISCELLANEOUS MILK FATS

Analysis	Goat milk[a]	Sheep milk[a]	Buffalo milk[b]	Camel milk[c]	Horse milk[a]
Composition of fatty acids					
Butyric......................	3.0	2.8	4.1	2.1	0.4
Caproic......................	2.5	2.6	1.4	0.9	0.9
Caprylic.....................	2.8	2.2	0.9	0.6	2.6
Capric.......................	10.0	4.8	1.7	1.4	5.5
Lauric.......................	6.0	3.9	2.8	4.6	5.6
Myristic.....................	12.3	9.7	10.1	7.3	7.0
Palmitic.....................	27.9	23.9	31.1	29.3	16.1
Stearic......................	6.0	12.6	11.2	11.1	2.9
Saturated, above C_{18}...........	0.6	1.1	0.9	—	0.3
Decenoic.....................	0.3	0.1	—	—	0.9
Dodecenoic...................	0.3	0.1	—	—	1.0
Tetradecenoic................	0.8	0.6	—	—	1.8
Hexadecenoic.................	2.6	2.2	—	—	7.5
Octadecenoic (oleic).........	21.1	26.3	33.2	38.9	18.7
Unsaturated, above C_{18}........	0.2	1.9	—	—	5.1
Octadecadienoic..............	3.6	5.2	2.6	3.8	7.6
Octadecatrienoic (linolenic)......	—	—	—	—	16.1
Characteristics					
Iodine value.................	28.8	36.7	33.5	40.8	84.3
Saponification equiv...........	233.7	244.5	240.4[d]	259.0	253.1
Reichert-Meissl value..........	23.2	26.2	32.2[d]	16.4	6.2
Polenske value................	7.2	3.6	2.0[d]	1.6	5.9
Kirschner value...............	15.6	17.6	28.4[d]	14.3	2.6

[a] T. P. Hilditch and H. Jasperson, *Biochem. J.*, *38*, 443–447 (1944).
[b] R. Bhattacharya and T. P. Hilditch, *Analyst*, *56*, 161–170 (1931).
[c] D. R. Dhingra, *Biochem. J.*, *28*, 73–78 (1934).
[d] Values given by C. P. Anantakrishnan, V. R. Bhalerao, and T. M. Paul, *Arch. Biochem.*, *13*, 389–393 (1947), for fat of iodine value 26.0.

buffaloes, goats, or sheep, or any mixture of these fats. It is to be noted that the milk fats of goats and sheep are distinguished from cow butterfat by their higher Polenske values and lower Kirschner values, but are distinguishable with difficulty from each other.[17]

Goat butterfat, as well as sheep butterfat, is characteristically very pale in color, due to a low carotene content, but is not correspondingly low in vitamin A. Typical carotene and vitamin A contents of summer goat butter, as reported by Gillam and Heilbron,[18] are 0.21 and 4.1 μg. per gram, respectively.

[17] F. T. van Voorst, *Chem. Weekblad*, *42*, 284–288 (1946).
[18] A. E. Gillam and I. M. Heilbron, *Biochem. J.*, *28*, 1082–1085 (1934).

C. Lauric Acid Oils

1. COCONUT OIL

Most of the characteristics which distinguish coconut oil (from *Cocos nucifera*) and other lauric acid oils from ordinary oils may be traced to a high content of low molecular weight fatty acids. Although referred to as an oil, coconut oil may be solidified at ordinary atmospheric temperature; its melting point is usually 24–27°C. (75–80°F.), and its solidifying
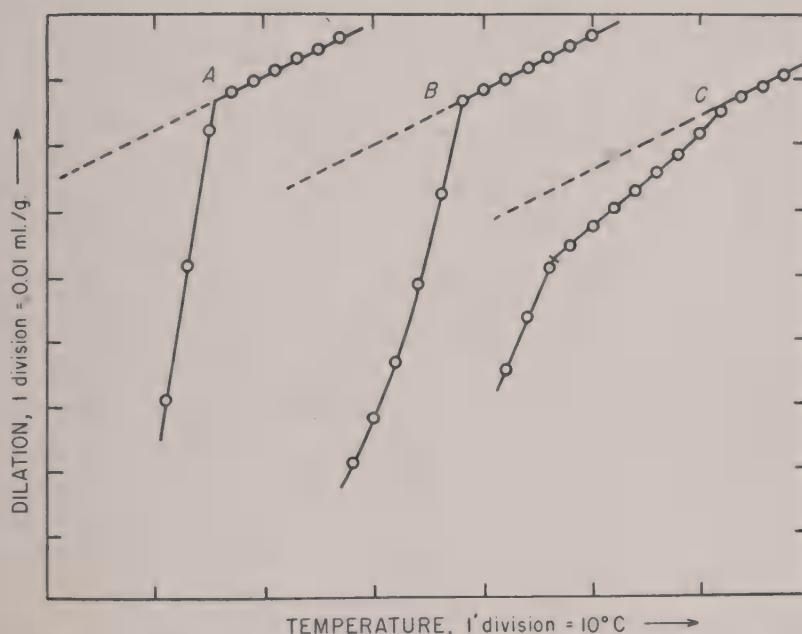
Fig. 13.   Dilatometric curves of different fats, illustrating abrupt melting of: (A) cocoa butter, and (B) coconut oil, as compared with gradual melting of: (C) lard.

point about 5°C. lower. The low melting point of coconut oil is not caused by a relatively high degree of unsaturation, as in the case of ordinary oils, but rather by the low molecular weight of its glycerides.

Unlike most fats, both natural and hydrogenated, coconut oil does not exhibit a gradual softening with increasing temperature, but is inclined to pass rather abruptly from a brittle solid to a liquid, within a temperature range of a relatively few degrees. The dilatometric curves of Figure 13 illustrate the difference in this respect between coconut oil and a fat such as lard. The reason for this peculiar melting behavior of coconut oil is readily apparent from consideration of its composition.

For a fat to melt and soften gradually, and thus exhibit an extended plastic range, it must be composed of a mixture of low-melting and high-

melting glycerides. While the melting points of the glycerides are determined by the manner in which the fatty acids are grouped within the glycerides, a wide range of melting in the glycerides is nevertheless dependent upon there being a corresponding range in the melting points of the component fatty acids. Coconut oil contains a greater variety of fatty acids than most oils, but this variety is occasioned by differences in the molecular weights of saturated acids, rather than by differences in the degree of unsaturation of the acids. Normally, about 75% of the total fatty acids of coconut oil consists of lauric, myristic, and palmitic acids. These acids melt at approximately 44°, 54°, and 63°C., respectively, hence there is a difference of but 19° between the melting points of the lowest and the highest members. On the other hand, the major fatty acids of high molecular weight fats are usually linoleic, oleic, palmitic, and stearic acids, which melt at −7°, 16°, 63°, and 70°C., with a difference of 77° between the lowest and the highest melting of the group. The relatively narrow melting range of the coconut oil fatty acids is reflected in the glycerides, and accounts for the limited plastic range of the latter.

Also unlike ordinary oils, coconut oil can be changed but little in melting point and consistency by hydrogenation. Even complete hydrogenation serves only to convert approximately 9% of combined oleic and linoleic acids to stearic acid; the saturated acids comprising 91% of the oil are of course unaffected by the process. Completely hydrogenated coconut oil has a melting point of about 111°F. (45.1°C). The narrow plastic range of coconut oil and the inability of the processor to modify greatly the physical properties of the oil by hydrogenation severely restrict the use of this oil in edible products. Coconut oil is seldom used as a major ingredient in shortening, and its short plastic range is even undesirable in margarine, although here the disadvantage is less, since the consistency of margarine is to some extent patterned after that of butter. Butter also has a comparatively short plastic range, due in part to the fact that it likewise contains a large proportion of low molecular weight fatty acids.

Since its unsaturation is low, coconut oil is extremely resistant to the development of rancidity. However, free acids are very noticeable in a coconut oil product if present in considerable amount, since they are sufficiently volatile and soluble to contribute a decided odor and flavor.

Crude coconut oil usually appears on the market with a somewhat higher free fatty acid content than ordinary vegetable seed oils. According to the trading rules commonly used in the United States the highest grade of coconut oil is required only to have a free acid content (calculated as oleic acid) under 3%, and much crude oil exceeds 5% in free acid content. The crude oil from carefully processed copra may have a Lovibond red color no higher than 2–3 units, although colors are more usually in the range of 10–20 units, and may even be as high as 50 units, or higher. The

color is reduced without difficulty by the usual refining and bleaching treatment, however. In addition to being low in pigments, high-grade coconut oil is very nearly free of phosphatides, gums, and other non-

TABLE 36

FATTY ACID COMPOSITION OF COCONUT AND PALM KERNEL OILS
(PER CENT BY WEIGHT)

Fatty acid	Coconut oil[a]	Coconut oil[b, c]	Palm kernel oil[b,d]
Caproic...............	0.8	Trace	—
Caprylic............	5.4	7.9	2.7
Capric...............	8.4	7.2	7.0
Lauric...............	45.4	48.0	46.9
Myristic............	18.0	17.5	14.1
Palmitic............	10.5	9.0	8.8
Stearic..............	2.3	2.1	1.3
Arachidic, etc.........	0.4	—	—
Oleic................	7.5	5.7	18.5
Palmitoleic..........	0.4	—	—
Linoleic.............	—	2.6	0.7

[a] H. E. Longenecker, *J. Biol. Chem.*, *130*, 167–177 (1939).
[b] G. Collin and T. P. Hilditch, *J. Soc. Chem. Ind.*, *47*, 261–269T (1928).
[c] Iodine value of this oil, 8.7; saponification equivalent, 217.9.
[d] Iodine value of this oil, 16.3; saponification equivalent, 230.2.

TABLE 37

A.O.C.S. STANDARD FOR COCONUT OIL

Specific gravity at 99°/15.5°C..........................	0.869–0.874
at 25°/15.5°C......................	0.917–0.919
Refractive index at 40°C.......................	1.448–1.450
Iodine value[a]...............................	7.5–10.5
Saponification value[a].......................	250–264
Unsaponifiable matter, %.....................	Not over 0.5
Titer, °C............................	20–24
Setting point, °C.......................	21.8–23
Reichert-Meissl value	6–8
Polenske value............................	15–18

[a] The addition of oils from the paring or rind of the kernel to "whole" coconut oil will raise the iodine value to 11–14, and lower the saponification value to 248–254.

glyceride substances commonly present in oils from seeds of annual plants.

The fatty acid composition of coconut oil is shown in Table 36. Collin and Hilditch[19] found coconut oil to consist of 84% trisaturated glycerides, 12% disaturated-monounsaturated glycerides, and 4% monosaturated-diunsaturated glycerides.

Coconut oil is distinguished from other fats and oils, except other lauric acid oils and butterfat, by the low average molecular weight of its fatty

[19] G. Collin and T. P. Hilditch, *J. Soc. Chem. Ind.*, *47*, 261–269T (1928).

acids, as evidenced by a high saponification value, and a low refractive index. The percentage of coconut oil in a mixture of coconut oil and tallow or other ordinary fats is usually calculated from the saponification value of the mixture. Andrews,[20] after examining a large number of samples of coconut oil fatty acids, listed the following average values for characteristics of the acids: saponification (neutralization) value, 268; iodine value, 10.1; titer, 23.3°C. These correspond to a saponification value and an iodine value of 253 and 9.5, respectively, for the glycerides. The content of unsaponifiable matter in coconut oil is usually 0.1–0.3%, and the average density is about 0.919 at 25°C., and 0.893 at 60°C. Values for the refractive index and the Reichert-Meissl, Polenske, and Kirschner values of coconut oil are given in Table 33.

The American Oil Chemists' Society recommended standard[21] for coconut oil is given in Table 37.

2. Palm Kernel Oil

Palm kernel oil, from kernels of the oil palm, *Elaeis guineensis*, is very similar to coconut oil in almost every respect. It has a somewhat higher iodine value than coconut oil, due to a higher content of unsaturated acids. However, the saturated fatty acids in which palm kernel oil is deficient, as compared with coconut oil, are principally the lowest melting members of the series, caproic and caprylic; hence its titer is but little different from that of coconut oil, and its melting point is only slightly (2–3°) higher. The fatty acid composition of a typical sample of palm kernel oil is recorded in Table 36. Collin and Hilditch[19] found this sample to contain 63% trisaturated, 26% disaturated-monounsaturated, and 11% monosaturated-diunsaturated glycerides.

Iodine values of about 16 to 23 have been recorded for palm kernel oil; the average iodine value of a large number of samples was found by Ellis and Hall[22] to be 18.6. Other average characteristics of palm kernel oil are approximately as follows: saponification value, 248; refractive index at 60°C., 1.4430; density at 60°C., 0.892; melting point, 26°C.; and unsaponifiable matter, 0.4%. The Reichert-Meissl, Polenske, and Kirschner values of palm kernel oil, which are slightly different from those of coconut oil, are listed in Table 33.

The A.O.C.S. recommended standard for palm kernel oil[21] is as follows:

Specific gravity at 99°/15.5°C.............................. 0.860–0.873
Refractive index at 40°C.................................. 1.449–1.452

[20] J. T. R. Andrews, *Oil & Soap, 10,* 165 (1933).
[21] See *Oil & Soap, 20,* 163–164 (1943).
[22] R. H. Ellis and E. M. Hall, *J. Soc. Chem. Ind., 38,* 128T (1919).

Iodine value. 14–22
Saponification value. 245–255
Unsaponifiable matter, %. . . . . Not over 0.8
Melting point, °C. 24–26
Setting point, °C. 20–26

As in the case of coconut oil, there are no color tests for palm kernel oil, hence it must be detected in admixture with butterfat or other fats and oils through its distinctive refractive index, saponification value, and Reichert-Meissl, Polenske, and Kirschner values. Its higher iodine value of course differentiates it from coconut oil, although it is virtually impossible to form any reliable estimate of the relative proportions of palm kernel and coconut oils in a mixture of the two.

Palm kernels are principally produced in Africa, and shipped to Europe for extraction of the oil. Although an effort is made to maintain the free fatty acid content of the kernels at a minimum, by drying the latter before shipment, a considerable time must necessarily elapse between shelling of the kernels and expression of the oil; hence palm kernel oil, like coconut oil, is ordinarily quite high in free fatty acid content.

TABLE 38

FATTY ACID COMPOSITION IN PER CENT BY WEIGHT OF AMERICAN
PALM KERNEL OILS

Characteristics and composition	Babassu[a]	Babassu[b]	Tucum[c]	Murumuru[d]	Ouricuri[e]	Cohune[f]
Iodine value.	16.1	15.1	15.8	11	14.7	9.8
Saponification value	249	—	241	242	256.9	251.0
Caproic.	0.2	—	—	—	1.8	Trace
Caprylic.	4.8	4.1	1.3	1.1	9.8	7.5
Capric.	6.6	7.6	4.4	1.6	8.2	6.6
Lauric.	44.1	45.1	48.9	42.5	45.8	46.4
Myristic.	15.4	16.5	21.6	36.9	9.0	16.1
Palmitic.	8.5	5.8	6.4	4.6	7.7	9.3
Stearic.	2.7	5.5	1.7	2.1	2.3	3.3
Arachidic.	0.2	0.7	—	—	0.1	—
Oleic.	16.1	11.9	13.2	10.8	13.1	9.9
Linoleic.	1.4	2.8	2.5	0.4	2.2	0.9

[a] F. L. Jackson and H. E. Longenecker, *Oil & Soap*, *21*, 73–75 (1944).
[b] H. Nobori and I. Ono, *J. Soc. Chem. Ind. Japan*, *43B*, 435–437 (1944).
[c] G. Collin, *Biochem. J.*, *27*, 1366–1372 (1933).
[d] M. Saraiva, *Mem. inst. chim. Rio de Janeiro*, No. 2, 5–19 (1929).
[e] R. S. McKinney and G. S. Jamieson, *Oil & Soap*, *15*, 172–174 (1938).
[f] T. P. Hilditch and N. L. Vidyarthi, *J. Soc. Chem. Ind.*, *47*, 35–37T (1928).

3. AMERICAN PALM KERNEL OILS

The Central and South American palms which have yielded kernel oils in sufficient quantity to be of some commercial importance include the *babassu* (*Orbygnia speciosa*), *tucum* (*Astrocaryum tucuma*), *murumuru* (*Astrocaryum murumuru*), *ouricuri* (*Syagrus coronata*), and *cohune* (*Attalea cohune*). The composition of samples of these oils, as reported by various observers, is in Table 38 (p. 137). All samples were of American origin except the tucum oil examined by Collin, which was from trees planted in Malaya.

TABLE 39

AVERAGE CHARACTERISTICS OF AMERICAN PALM KERNEL OILS

Analysis	Babassu	Tucum	Murumuru	Ouricuri	Cohune
Iodine value	15.5	9–14	11	15	10–14
Saponification value	247	230–250	242	257	250–255
Density, 60°C	0.893	0.893	0.893	0.898	0.893
Refractive index, 60°C	1.443	1.443	1.445	1.440	1.441
Unsaponifiable matter, %	0.2–0.5	0.3	0.3	0.3	0.4
Melting point, °C	22–26	30	32	18	24
Titer, °C	23	27	—	—	21
Reichert-Meissl value	5–7	4	3	6	7
Polenske value	10–12	6	—	18	14

The American palm kernel oils are generally similar to the kernel oil of the African or oil palm. However, tucum and murumuru oils, it is to be noted, are somewhat higher melting than palm kernel oil, and ouricuri oil differs from both coconut and palm kernel oils in its relatively high content of caproic, caprylic, and capric acids, and its correspondingly lower melting point, and higher Reichert-Meissl value. These oils are all generally similar to coconut and palm kernel oils in free fatty acid content, appearance, plastic range, etc., and are used for the same purposes. Characteristics of American palm kernel oils are listed in Table 39.

D. Vegetable Butters

The vegetable butters are unique in a number of respects among fats and oils. They have the property of melting very sharply; in the case of cocoa butter and Borneo tallow, softening and melting occur over an even more restricted range of temperatures than in lauric acid oils. However, the short plastic range of the vegetable butters is not due to the presence of low molecular weight fatty acids, but arises from the peculiar configuration of the glycerides in these fats. They consist of relatively simple mixtures of glycerides; in some cases they are apparently composed

preponderantly of either a single glyceride or of two or more glycerides of very nearly identical melting point. It has been estimated that over 70% of the glycerides of cocoa butter, for example, are composed of a single oleic acid radical in combination with stearic or palmitic acid, or both. Probably about half of the glycerides of cocoa butter consist of oleopalmitostearin. The preponderance of a single glyceride not only causes the fat to melt sharply, but also confers upon it distinctive habits of melting and crystallization. Some of the vegetable butters exhibit the phenomenon of polymorphism to a pronounced degree; the consistency and melting point of cocoa butter in particular is variable according to the conditions under which it has been solidified or stored subsequent to solidification.

Due to the extensive researches of Hilditch and co-workers, compositions of the more common vegetable butters are known with considerable exactness, not only with respect to the component fatty acids, but also with respect to the different classes of glycerides. Table 40 contains data on the composition of some of the better known vegetable butters.

TABLE 40

COMPOSITION OF SOME VEGETABLE BUTTERS

Analysis	Cocoa butter[a]	Borneo tallow[b]	Shea butter[c]	Mowrah fat, (illipé fat)[d]
Iodine value	36.7	33.2	59.1	63.9
Fatty acids (wt. %)				
Palmitic	24.4	18.0	5.7	23.7
Stearic	35.4	43.3	41.0	19.3
Arachidic	—	1.1	—	—
Oleic	38.1	37.4	49.0	43.3
Linoleic	2.1	0.2	4.3	13.7
Glycerides (mol %)				
Palmitostearins	2	5	5	1
Monounsaturated palmitostearin	52	31	—	27
Monounsaturated dipalmitin	6	8	—	1
Monounsaturated distearin	19	40	34	—
Diunsaturated stearin	12	13	45	30
Diunsaturated palmitin	9	3	11	41
Triunsaturated	—	—	5	—

[a] T. P. Hilditch and W. J. Stainsby, *J. Soc. Chem. Ind.*, *55*, 95–101T (1936).
[b] W. J. Bushnell and T. P. Hilditch, *J. Soc. Chem. Ind.*, *57*, 447–449 (1938).
[c] T. G. Green and T. P. Hilditch, *J. Soc. Chem. Ind.*, *57*, 49–53 (1938).
[d] T. P. Hilditch and M. B. Ichaporia, *J. Soc. Chem. Ind.*, *57*, 44–48T (1938).

1. COCOA BUTTER

Cocoa butter is a pale yellow solid with the characteristic odor and flavor of the cocoa bean, which is obtained from the tropical plant *Theobroma cacao*. It is brittle at temperatures below about 80°F. (26.7°C.);

slightly above this temperature it softens and melts. The melting point of cocoa butter depends upon the crystal modification in which it exists. A sample which has been quickly chilled to an unstable crystal form will liquefy if suddenly heated to a temperature as low as 26–30°C. However, if heating is carried out gradually, to permit transformation of the fat to its highest melting form, the melting point will usually be 35–36°C. Below its softening point cocoa butter is not greasy to the touch; its combination of hardness and nongreasiness at ordinary temperatures with a melting point below the temperature of the human body makes it pre-eminently suitable as a coating fat for confections, in which it is ordinarily blended with chocolate. Since its characteristic flavor is desirable in confections, cocoa butter is subjected to the processing treatments of refining, deodorization, etc., only when it is desired to reclaim fat whose quality has suffered from age or from damage to the cocoa beans. As compared to ordinary fats and oils, cocoa butter is extremely resistant to deterioration through oxidation or the development of rancidity.

The composition of a representative sample of cocoa butter is shown in Table 40. Average characteristics of cocoa butter are approximately as follows: iodine value, 38; saponification value, 194; refractive index at 60°C., 1.4490; density at 60°C., 0.8825; melting point, 34–35°C.; titer, 49°C.; unsaponifiable matter, 0.6%. Cocoa butter of good quality usually contains 0.5 to 1.0% of free fatty acids.

The admixture of foreign fats in cocoa butter will generally be evident from their effect on the melting characteristics of the fat, as determined by dilatometry or other methods, or from their effect on the turbidity and solidification tests described respectively by Jamieson[23] and Jensen.[24] The admixture of lauric acid oils or pressed "stearines" derived from such oils will increase the saponification and Polenske values of the fat. It is difficult to determine when cocoa butter has been adulterated with Borneo tallow because of the great similarity between the two fats. For the detection of this fat in cocoa butter, the turbidity and solidification tests mentioned above are particularly recommended.

Following is the A.O.C.S. recommended standard for cocoa butter.[25]

Specific gravity at 99°/15°C.	0.856–0.864
Refractive index at 40°C.	1.453–1.458
Iodine value	35–40
Saponification value	190–200
Unsaponifiable matter, %	Not over 1.0
Melting point (open capillary), °C.	28–36
Titer, °C.	45–50

[23] G. S. Jamieson, *Vegetable Fats and Oils.* 2nd ed., Reinhold, New York, 1943, pp. 43–44.
[24] H. R. Jensen, *The Chemistry, Flavoring and Manufacture of Chocolate Confectionery and Cocoa,* Blakiston, Philadelphia, 1931.
[25] See *Oil & Soap, 19,* 140 (1942).

2. Other Vegetable Butters

Borneo tallow, from the East India and Malayan plant *Shorea stenoptera,* is also known as "green butter," from its characteristic greenish tinge; it resembles cocoa butter more closely than any other fat. Published values for its various characteristics vary considerably, and overlap the values given above for cocoa butter. However, it would appear that Borneo tallow may ordinarily be about 5 units lower in iodine value than the average cocoa butter and 2° to 3°C. higher in both melting point and titer.

Shea butter, from the African plant *Butyrospermum parkii,* is much more unsaturated than cocoa butter or Borneo tallow and is correspondingly softer and less brittle. It is said to be suitable for use as a coating fat only after separation of the more liquid portions by pressing. Shea butter has a characteristically high content of unsaponifiable matter (3–10%). The iodine and saponification values of this fat depend to a great extent upon the amount of unsaponifiable material present. Iodine values of 56 to 65 and saponification values of 178 to 189 are quoted in the literature. The melting point is said to range from 33° to 42°C., and the titer from 52° to 53.5°C.

Mowrah fat, or illipé butter, which is obtained from the Indian plant *Bassia longifolia,* resembles Shea butter in being relatively unsaturated, and correspondingly soft. It is said to be used chiefly for candle- and soap-making. A sample of crude fat examined by Hilditch and Ichaporia[26] had an iodine value of 63.9 and a saponification equivalent of 290.2, and contained 2.1% of unsaponifiable matter and approximately 10% of free fatty acids.

Hilditch and Priestman[27] found a sample of *Chinese vegetable tallow* (*Stillingia sebifera*) from China to have the following fatty acid composition: lauric, 2.5%; myristic, 3.6%; palmitic, 57.6%; stearic, 1.8%; and oleic, 34.5%. A refined sample of tallow from trees grown in the southern United States was examined at the same time and found to contain the following acids: lauric, 1.2%; myristic, 2.9%; palmitic, 63.1%; stearic, 3.2%; and oleic, 29.6%. The latter sample had an iodine value of 22.1, a saponification equivalent of 275.4 (saponification value, 204), and a setting point of 48.2°C.

Nutmeg butter (*Myristica officinalis*) is characterized by a very high content of myristic acid, the fatty acid composition of this fat, as reported by Collin and Hilditch,[28] being as follows: lauric, 1.5%; myristic, 76.6%; palmitic, 10.1%; oleic, 10.5%; and linoleic, 1.3%. Since nutmeg butter

[26] T. P. Hilditch and M. B. Ichaporia, *J. Soc. Chem. Ind.,* 57, 44–48T (1938).
[27] T. P. Hilditch and J. Priestman, *J. Soc. Chem. Ind.,* 49, 397–400T (1930).
[28] G. Collin and T. P. Hilditch, *J. Soc. Chem. Ind.,* 49, 141–143 (1930); *Biochem. J.,* 23, 1273–1289 (1929).

contains a very high proportion of essential oils and other unsaponifiable material, neither the iodine value nor the saponification value are indicative of the composition of the glyceride portion. The original fat examined by the above investigators had an iodine value of 61, and contained 17.7% of unsaponifiable matter. After the removal of 25% of volatile matter by steam distillation, the residual oil had an iodine value of 46.6 and a saponification equivalent of 295.

A sample of refined *ucuhuba butter* (*Virola surinamensis, sebifera*) from Brazil was examined by Atherton and Meara,[29] who reported the following composition for the fatty acids; capric acid, 0.5%; lauric acid, 14.8%; myristic acid, 72.5%; palmitic acid, 4.9%; and oleic acid, 6.3%. The composition of the glycerides was estimated to be as follows: trimyristin, 43%, laurodimyristin, 31%; oleolauromyristin, 12%; and lauromyristopalmitin, 10%. The fat had an iodine value of 9.9 and a saponification equivalent of 246.1 (saponification value, 228). The melting point of ucuhuba butter is 40–47°C.[1b]

E. Animal Fats

1. Lard

Lard or hog fat appears on the market in a number of different grades, according to the part of the animal from which it is derived and the method employed in rendering it. The greater portion of the lard produced in the United States consists of *prime steam* lard, which includes fat from all parts of the animal except the leaf fat, and is rendered by a wet method. A certain amount of dry-rendered lard is also produced, comparable to prime steam lard in composition, but rendered by a dry process. *Neutral* lard, wet-rendered at a low temperature from selected stock, especially for margarine manufacture, was once an important article of commerce, but has been produced in only small quantity since hydrogenated vegetable and whale oils have become generally available. *Leaf* lard is dry-rendered from the hard internal fat of the hog, and is firmer and lower in iodine value than other lards. Small amounts of *kettle-rendered* lard other than leaf lard are also produced. According to government regulations in the United States, the fat rendered from certain less desirable packing house products may not be called lard, but must be labeled and sold as *rendered pork fat*. Rendered pork fat is usually darker in color than lard, and may have a higher free fatty acid content, but is often more resistant to the development of rancidity than ordinary grades of lard.

The composition, characteristics, and consistency of lard vary greatly according to the feed of the hogs as well as the part of the animal from

[29] D. Atherton and M. L. Meara, *J. Soc. Chem. Ind.*, *58*, 353–357 (1939).

which it is taken. American prime steam lard has an average iodine value of about 68; the average iodine value of American leaf lard is in the neighborhood of 58. European lard is generally considerably lower in iodine value and firmer than the lard produced in the United States. Lard from peanut-fed hogs raised in the southern United States is very soft, and often has an iodine value of 85 or more. The Oil Characteristics Committee of the A.O.C.S. has recommended the following standard for North American lard:[25]

Specific gravity at 99°/15.5°C.............................. 0.858–0.864
Refractive index at 40°C. (Zeiss)......................... 45–52
Iodine value... 46–70
Saponification value.. 195–202
Unsaponifiable matter, %.................................... Not over 1.0
Titer, °C.. 36–42
Grades: Edible-Neutral (Nos. 1 and 2), Leaf, Choice Kettle, Prime Steam.
Tests: F.F.A. max. 1%, peroxide number (milliequivalents) 5 max.
Tristearin test for purity:
 1. Bömer number (ether) not less than 71.
 2. A.O.C.S. (acetone) not less than 73.

Since the characteristics of lard will be fully discussed in a later chapter devoted to plastic shortening agents, attention here will be directed mainly to certain minor fatty acids of lard, and the glyceride structure of this fat. In addition to the stearic and palmitic acids commonly reported, lard contains a small amount of myristic acid (1–2%), a fractional percentage of lauric acid, and a trace of capric acid.[30] An appreciable part of the monoethenoid acids ordinarily reported as oleic acid in lard actually consists of tetradecenoic and hexadecenoic acids, with a trace of dodecenoic. Unsaturated acids above C_{18} (probably C_{20} and C_{22}) amount to 1–2%. These appear to consist for the most part of a diethenoid C_{20} acid,[30] although arachidonic acid is present to the extent of 0.2–0.6%.[31,32] Detailed analyses of typical American and European lards are presented in Table 41. These apply to lard from hogs on more or less normal feeds. Lard of unusual composition is readily produced by feeding hogs on high-fat diets; for example, Shorland and de la Meara[32a] reported 13% myristic acid in lard from copra-fed hogs. For information on the effects of peanut and soybean feeding, Chapter VIII.

The presence of beef fat in lard may be recognized by the Bömer test,[33] which depends upon the fact that the high-melting palmitodistearin

[30] P. B. D. de la Meara and F. B. Shorland, *Analyst*, 69, 337–339 (1944).
[31] J. B. Brown and E. M. Deck, *J. Am. Chem. Soc.*, 52, 1135–1138 (1930).
[32] B. W. Beadle, H. R. Kraybill, and L. A. Stricker, *Oil & Soap*, 22, 50–51 (1945).
[32a] F. B. Shorland and P. B. D. de la Meara, *J. Agr. Soc.*, 35, 39–43 (1945).
[33] A. Bömer, R. Limprich, R. Krönig, and J. Kuhlmann, *Z. Untersuch. Nahr.-Genussm.*, 26, 559–618 (1913). V. C. Mehlenbacher, editor, *Official and Tentative Methods of the American Oil Chemists' Society*, 2nd ed., Chicago, 1946 (revised annually), Official Method Cb 5-40.

CHARACTERISTICS AND COMPOSITION OF AMERICAN AND EUROPEAN LARDS

Analysis	European lard[a]	American lard[b]
Characteristics		
Iodine value	59.8	68.0
Saponification equivalent	285.9	288.1
Saponification value	196	195
Melting point, °C., Wiley	—	36.5
Unsaponifiable matter, %	0.2	0.35
Fatty acid composition (wt. %)		
Myristic	1.3	—
Palmitic	28.3	—
Stearic	11.9	—
Total saturated	*41.5*	*36.1*
Tetradecenoic	0.2	—
Hexadecenoic	2.7	—
Oleic	47.5	49.6
Linoleic	6.0	12.8
Trienoic (calc. as linolenic)	—	0.8
Tetraenoic (calc. as arachidonic)	—	0.4
C_{20} and C_{22} unsaturated	2.1	—
Total unsaturated	*58.5*	*63.6*
Glyceride composition (mol %)		
Tripalmitin	1	—
Palmitodistearin	2	—
Stearodipalmitin	2	—
Total trisaturated	*5*	*1.9*
Dipalmito-unsaturated	5	—
Distearo-unsaturated	—	—
Palmitostearo-unsaturated	27–34	—
Total disaturated	*32–39*	*25.7*
Palmitodiolein	46–53	—
Stearodiolein	0–7	—
Total monosaturated	*46–60*	*54.4*
Triunsaturated	3–10	18.0

[a] T. P. Hilditch, C. H. Lea, and W. H. Pedelty, *Biochem. J.*, *33*, 493–501 (1939). T. P. Hilditch and W. H. Pedelty, *ibid.*, *34*, 971–979 (1940).

[b] R. W. Riemenschneider, F. E. Luddy, M. L. Swain, and W. C. Ault, *Oil & Soap*, *23*, 276–282 (1946). Values for glyceride composition are not of unquestioned reliability, and are to be regarded as estimates only.

in the two fats consists of each case of a different isomer. However, this test is invalidated by the presence of hydrogenated lards in the fat.[34]

[34] L. M. Tolman and A. A. Robinson, *Oil & Soap*, *9*, 13 (1932).

Lard may be detected in vegetable oil shortenings by spectrophotometric means, through its content of tetraethenoid (arachidonic) acids.[32]

2. Greases

The term "grease" refers to the softer inedible fats used principally by soapmakers. Inedible tallows and greases produced by meat packing houses may contain either hog or beef fat. However, they are defined in terms of their hardness rather than their origin, a fat with a titer below 40°C. being considered a grease, and a fat with a titer over 40° being classed as an inedible tallow. Packing house grease is produced in several different grades, according to the color, titer, free fatty acid content, and "MIU" content of the material.

White grease is quite similar to lard. In the case of the highest "Choice" grade, its classification as an inedible product may arise chiefly from aesthetic considerations, as it is sterile and may be refined to entire freedom from objectionable impurities, even though it is rendered from inedible materials. The addition of denaturants at the packing houses according to government regulations has served to prevent the diversion of white grease to edible uses in the United States, but in the past there have been instances in which white grease has been exported to Europe and illegally refined and sold as a food.

Yellow grease is of lower quality than white grease. It is yellowish rather than white in the solidified form, and has a free fatty acid content up to 15%. *Brown grease* is the lowest grade of packing house grease, being darker in color and higher in free fatty acid content than yellow grease (up to 50%).

There are a number of other greases, which may or may not consist largely of hog fat. These include *glue grease,* a by-product of glue manufacture, *bone grease,* which is derived from the processing of bones for gelatin, glue, etc., *tankage grease,* a low-grade product extracted from animal wastes, *house grease,* which is the waste cooking fat from restaurants and hotels, and *garbage grease,* which is recovered from collections of city garbage. Low-grade fats in the grease class are obtained in relatively small amounts from various other sources, such as the degreasing of hides for the manufacture of patent leather and leather upholstery, the disposition of spent tinning and terne plating oils, etc. The lower grade greases are in general not used for any industrial purpose as such, but serve as raw materials for the production of distilled fatty acids.

Regulations of the U. S. Department of Agriculture require that white grease or other inedible fats which have the physical properties of edible fats be denatured by the addition of petroleum distillates directly to the vessel in which rendering is carried out.

Since greases are principally used in the manufacture of soaps or fatty acids, one of their most important characteristics is their actual content of saponifiable fatty material. The nonfatty material in a grease is measured by the so-called MIU, which is the combined content of moisture, insoluble impurities, and unsaponifiable matter. The MIU, together with the color and free fatty acids content, figures prominently in the trading rules applied to greases, allowances in the prices of the different grades being made for an MIU above a fixed maximum value.

The commonly recognized standards for the different grades of greases are shown in the accompanying table.

Grade	Min. titer, °C.	Max. FFA, %	Max. FAC color	Max. MIU, %
Choice White...............	37.0	4	11	1
White A...................	37.0	8	15	1
White B...................	36.0	10	19 or 11C	2
Yellow....................	36.0	15	37	2
House....................	37.5	20	39	2
Brown....................	38.0	50	None	2
No. 1 Glue or Fleshing......	37.0	15	15	2
No. 2 Glue or Fleshing.......	37.0	40	21	2

3. TALLOWS AND TALLOW DERIVATIVES

Characteristics and compositions of various tallows are shown in Table 42. The beef tallows with the highest and lowest iodine values represent extremes in the composition of this fat; average packing house tallow in the United States has an iodine value of about 42. The statement has frequently been made that South American tallows are harder and lower in iodine value than North American tallows, because they are derived from grass-fed rather than grain-fed animals. However, in the author's experience there are no consistent differences in either iodine values or firmness among edible tallows from the United States, South America, Australia, and New Zealand (see Table 67, page 238). There is, in fact, considerable evidence that the body fat of cattle, unlike that of swine, is relatively little affected by the feed of the animal.[35] On the other hand, the environment of the animal appears to influence the composition of the fat, with warm temperatures tending to reduce the unsaturation. Tallow from Indian cattle is reported[36] to be consistently as low as 26–31 in iodine value. As in the hog, the softest and most unsaturated fat is formed near the skin, and the hardest around the internal organs; hence

[35] See, for example, B. H. Thomas, C. C. Culbertson, and F. Beard, *Rec. Proc. 27th Ann. Meeting Am. Soc. Animal Prod., 1934.* 193–199.
[36] K. T. Achaya and B. N. Banerjee, *Current Sci., 15,* 23–24 (1946).

the consistency and unsaturation of commercial tallows is determined to a considerable extent by the trimming practices followed in the particular establishment in which the fat is rendered.

TABLE 42

CHARACTERISTICS AND FATTY ACID COMPOSITION OF
BEEF, MUTTON, AND GOAT TALLOWS

Analysis	Beef[a] (N. American)	Beef[b] (English)	Beef[c] (N. American)	Beef[b] (Indian)	Mutton[d] (English)	Goat[e] (Indian)
Characteristics						
Iodine value	49.5	44.7	40.2	—	41.2	33.5
Saponification equiv.	284.2	—	286.4	—	285.4	282.0
Saponification value	197	—	196	—	197	199
Titer, °C	42.3	—	—	—	—	46.2
Unsaponifiable, %	—	—	0.74	—	—	0.18
Composition, fatty acids (wt. %)						
Lauric	—	0.2	—	0.2	—	3.5
Myristic	6.3	3.1	—	3.7	4.6	2.1
Palmitic	27.4	24.9	—	37.1	24.6	25.5
Stearic	14.1	24.1	—	29.4	30.5	28.1
Arachidic	—	0.8	—	1.2	—	2.4
Total saturated	*47.8*	*53.1*	*55.5*	*71.6*	*59.7*	*61.6*
Tetradecenoic	—	0.4	—	0.4	—	—
Hexadecenoic	—	2.4	—	1.0	—	—
Oleic	49.6	41.8	41.4	25.9	36.0	38.4
Octadecadienoic	2.5	1.8	1.8	0.9	4.3	—
C_{20}–C_{22} unsaturated	—	0.5[f]	0.5	0.2	—	—
Total unsaturated	*52.1*	*46.9*	*43.7*	*28.4*	*40.3*	*38.4*
Composition, glycerides (mol %)						
Trisaturated	13.9	15.5	14.7	—	26	29.2
Disaturated	22–54	31	45.9	—	30–52	31–51
Monosaturated	0–64	53	37.1	—	0–44	0–40
Triunsaturated	0–32	—	2.2	—	—	0–20

[a] A. Banks and T. P. Hilditch, *Biochem. J.*, *25*, 1168–1182 (1931).
[b] T. P. Hilditch and H. E. Longenecker, *Biochem. J.*, *31*, 1805–1819 (1937).
[c] R. W. Riemenschneider, F. E. Luddy, M. L. Swain, and W. C. Ault, *Oil & Soap*, *23*, 276–282 (1946). Analysis in terms of glycerides is approximate only.
[d] G. Collin, T. P. Hilditch, and C. H. Lea, *J. Soc. Chem. Ind.*, *48*, 46–50 (1929).
[e] D. R. Dhingra and D. N. Sharma, *J. Soc. Chem. Ind.*, *57*, 369–370 (1938).
[f] Total triethenoid acids.

Mutton tallow is ordinarily a little harder and lower in iodine value than beef tallow, and hence the mutton tallow of Table 42 may be regarded as a relatively soft sample. The greater hardness of this fat, as compared with beef tallow, may be at least in part a result of greater proportions of the harder internal fat tissues finding their way into the rendering

kettle. Wright and Thompson,[36a] from the results of titer tests carried out on thousands of samples from New Zealand slaughter houses, were able to discern a pronounced gradation in hardness (and, presumably, unsaturation) according to the latitude in which the sheep were raised. Average titers (°C.) for different mean latitudes south were as follows:

Latitude	40.0°	41.5°	43.5°	44.5°	46.0°
Caul and kidney fat........	47.9	46.1	45.8	45.1	44.7
Intestinal and visceral fat...	44.1	43.8	43.0	42.8	42.7

It will be seen that, in common with many other vegetable and animal fats and oils, the fat becomes increasingly unsaturated as the climate becomes colder.

Monthly averages for the titers of New Zealand mutton tallows from the different locations varied from a high of 49.1° and a low of 42.5° for the caul and kidney fat to a high of 45.4° and a low of 41.5° for the intestinal and visceral fat. In addition to the variations previously mentioned, it was noted that the fat from mature animals was harder than that from young animals, and that the fat of the male was usually harder than that of the female.

Goat tallow is even harder and less unsaturated than beef tallow. The characteristics noted for the goat tallow of Table 42 are all within the range of values quoted by Pritzker and Jungkunz[37] for Swiss goat tallow, which varied in iodine value from 32.4 to 38.6.

In addition to the fatty acids reported in the table, the presence of traces of highly unsaturated C_{20} and C_{22} acids has been reported in both beef and mutton tallow by Hilditch and co-workers.[1a]. There are also mono- and diethenoid acids of 20 carbon atoms. Recently Knight and co-workers[38] have established that the nonconjugated acids of two and three double bonds in tallow (2.2% and 0.46%, respectively, in a typical sample) are principally normal linoleic and linolenic acids, identical with those in vegetable oils, and not isomers, as was believed previously.

Following is the standard for pure beef tallow recommended by the Oil Characteristics Committee of the A.O.C.S.:[25]

Specific gravity at 99/15.5°C............................	0.860–0.870
Refractive index at 40°C. (Zeiss).........................	46–49
Iodine value...	35–48
Saponification value.....................................	193–202
Unsaponifiable matter, %.................................	Not over 0.8
Titer, °C..	40–46

The more common grades of commercial tallow, which may or may not consist wholly of beef or mutton fat, are defined as follows:

[36a] A. M. Wright and I. Thompson, *J. Soc. Chem. Ind.*, *47*, 13–14T (1928).
[37] J. Pritzker and R. Jungkunz, *Pharm. Acta Helv.*, 7, 48–53 (1932).
[38] H. B. Knight, E. F. Jordan, Jr., and D. Swern, *J. Biol. Chem.*, *164*, 477–482 (1946).

Grade	Min. titer, °C.	Max. FFA, %	Max. FAC color	Max. MIU. %
Edible	41.5	1	5	1
Fancy	41.5	4	7	1
Choice	41.0	5	9	1
Prime or Extra	40.5	6	13 or 11B	1
Special	40.5	10	19 or 11C	2
No. 1	40.0	15	33	2
No. 3	40.0	20	39	2
No. 2	40.0	35	None	2
Naphtha Extracted Bone	40.0	50	None	2

TABLE 43

CHARACTERISTICS AND COMPOSITION OF NEATSFOOT OIL[a]

Characteristics	
Iodine value	73.3
Saponification equivalent	286.3
Saponification value	196
Free fatty acids content, %	0.7
Unsaponifiable matter, %	0.3
Refractive index at 40°C	1.4610
Fatty acid composition, wt. %	
Myristic	0.7
Palmitic	16.9
Stearic	2.7
Arachidic	0.1
Tetradecenoic	1.2
Hexadecenoic	9.4
Oleic	64.4
Octadecadienoic	2.3
Octadecatrienoic	0.7
Unsaturated C_{20}–C_{22}	1.6
Approximate glyceride composition, mol %	
Palmitic-palmitic-oleic	0.6
Palmitic-stearic-oleic	6.6
Total disaturated	*7.2*
Palmitic-oleic-oleic	35.2
Palmitic-hexadecenoic-oleic	10.2
Palmitic-oleic-polyethenoid	4.5
Stearic-oleic-oleic	4.2
Total monosaturated	*54.1*
Oleic-hexadecenoic-polyethenoid	2.2
Oleic-oleic-hexadecenoic	23.2
Oleic-oleic-polyethenoid	7.7
Oleic-oleic-oleic	5.6
Total triunsaturated	*38.7*

[a] T. P. Hilditch and R. K. Shrivastava, *J. Soc. Chem. Ind.*, *67*, 139–142 (1948).

Edible tallow must, of course, be rendered from B.A.I.-approved edible stock.

Neatsfoot oil is a special inedible fat of low melting point (liquid or substantially liquid at ordinary temperatures) rendered from the feet of cattle. A complete analysis appears in Table 43. The A.O.C.S. recommended standard for neatsfoot oil is as follows:[25]

Specific gravity at 25°/25°C.	0.907–0.912
Refractive index at 25°C.	1.464–1.465
Iodine value.	66–76
Saponification value.	190–199
Unsaponifiable matter, %.	Not over 1
Titer, °C.	20–30
Pour point (A.S.T.M.), °F.	20–35

Oleostock is a high grade of inedible tallow prepared by low-temperature wet rendering of the fresh internal fat of beef carcasses. This fat has a light, yellow color, a mild, pleasant flavor, and a free fatty acid content of usually less than 0.2%. It generally has an iodine value between 36 and 40, a titer of 44° to 46°C., and a melting point of about 48°C. It is pressed to yield *oleo oil* and *oleostearine*, a hard fat with an iodine value of about 25, and a titer of about 50°C. Most oleo oil has an iodine value of 44 to 48 and a titer of 41° to 42°C. Usually it melts at about 32° to 34°C. (90–94°F.), but is quite brittle at refrigerator temperatures. Its plastic range is thus very short. The free fatty acid contents of oleostearine and oleo oil are comparable to that of the oleo stock from which they are prepared, but most of the yellow pigments (carotene) of the oleo stock appear in the oil rather than the stearine. Oleostearine as it is prepared commercially often contains a sufficient amount of water and water-soluble substances remaining from the rendering operation to make it susceptible to deterioration through mold growth.

F. Oleic-Linoleic Acid Oils

1. COTTONSEED OIL[39]

Crude cottonseed oil, derived from the plants *Gossypium hirsutum* (American) or *Gossypium barbadense* (Egyptian), has a strong, characteristic flavor and odor and a dark, reddish brown color from the presence of highly colored material extracted from the seed. Its free fatty acid content and general quality depend to a considerable extent upon the weather prevailing during the time that the cotton stands in the field after coming

[39] For detailed information on the characteristics and composition of cottonseed oil, see A. E. Bailey, ed., *Cottonseed and Cottonseed Products*, Interscience, New York, 1948.

to maturity. Hence the quality of crude oil will vary in any given locality from year to year, being highest in dry seasons, and lowest when the seed is exposed to wet weather in the fields, or handled or stored with a high moisture content. The free fatty acid content of the best North American oil will vary from 0.5 to 1.0%, although oil containing 1.5 to 3.0% of free acids is not uncommon, and the free acid content of oil from wet or damaged seeds may be as high as 5% or higher.

In the United States, where elaborate trading rules have been evolved for dealing in cottonseed oil, the grade and price of the oil are not established from the characteristics of the crude oil, but are based upon the yield of oil obtained by a standard refining test, and the color of the refined oil. The crude oil refines by caustic soda treatment to a relatively light color, i.e., good oil may readily be refined to a color on the Lovibond scale of 35 yellow and 4 to 7 red. As the free fatty acid content of the oil increases, there is a corresponding increase in the refining loss, coupled with a more or less progressive increase in the color of the refined oil. Within comparatively wide limits, however, the quality of the refined oil, with respect to its stability, flavor, etc. bears little relation to the free fatty acid content of the crude oil.

Cottonseed oil contains more saturated fatty acids than most oils of an equivalent iodine value hence its titer is high and the oil itself will become partially solidified upon storage at temperatures below 50° to 60°F. Cloud and pour points of refined cottonseed oil by the A.S.T.M. method are about 33° to 38°F. and 25° to 30°F., respectively.[40,41]

Cottonseed oil from the Delta region of the lower Mississippi valley will average very close to 108 in iodine value, seldom being above 111 or below 105. Oil of this iodine value will contain about 25% saturated acids, 25% oleic acid, and 50% linoleic acid, and will have a saponification value of about 195 and titer of about 34.5°C. Texas cottonseed oil is consistently less unsaturated than Delta oil, its iodine value averaging in the neighborhood of 103. Cottonseed oil from southeastern United States is similar in composition to Delta oil. Oil from other cotton-producing regions of the world appears to generally have characteristics falling within the range of North American cottonseed oils, although Jamieson[1b] states that oil from Indian seed averages as high as 112 to 116 in iodine value.

Characteristics and compositions of cottonseed oils from a variety of sources are reported in Table 44. A detailed analysis of cottonseed oil, as given by Hilditch and Maddison,[42] including estimates of the minor fatty acids and the glyceride composition, is presented in Table 45.

[40] A. E. Bailey, R. O. Feuge, E. A. Kraemer, and S. T. Bauer, Oil & Soap, 20, 129–132 (1943).
[41] See Oil & Soap, 15, 245 (1938); 16, 141 (1939).
[42] T. P. Hilditch and L. Maddison, J. Soc. Chem. Ind., 59, 162–168 (1940).

<div align="center">TABLE 44</div>

CHARACTERISTICS AND APPROXIMATE COMPOSITION OF REFINED COTTONSEED OIL FROM DIFFERENT SOURCES

Analysis	U. S. (Georgia)[a]	U. S. (Texas)[a]	Sudan (Africa)[a]	Brazil[a]	China[b]
Iodine value	109.2	103.0	101.8	105.5	104.7
Refractive index at 50°C	1.46260	1.46413	1.4636	1.4642	—
Saponification value	194.6	193.0	189.4	192.0	193.0
Acetyl value	9.7	12.0	12.2	11.4	—
Unsaponifiable matter, %	0.54	0.45	0.83	0.77	1.51
Reichert-Meissl value	0.45	0.40	0.9	2.0	—
Polenske value	0.53	0.30	0.2	0.4	—
Titer, °C	34.8	32.8	37.0	34.6	31.0
Cloud point (A.S.T.M.), °F	30	38	—	—	—
Pour point (A.S.T.M.), °F	25	30	—	—	—
Saturated acids	24.0	24.2	27.6	25.6	—
Oleic acid	24.6	27.6	25.4	25.4	—
Linoleic acid	51.4	48.2	46.2	48.2	—

[a] *Oil & Soap*, *15*, 245 (1938); *16*, 141 (1939).
[b] P. E. Ronzone, *Oil & Soap*, *13*, 165–167 (1936).

<div align="center">TABLE 45</div>

COMPOSITION OF COTTONSEED OIL[a]

Analysis	Per cent by weight
Iodine value	105.0
Saponification equivalent	286.4
Fatty acids (wt. %)	
Myristic	1.4
Palmitic	23.4
Stearic	1.1
Arachidic	1.3
Tetradecenoic	0.1
Hexadecenoic	2.0
Oleic	22.9
Linoleic	47.8
Glycerides (mol %)	
Trisaturated	0.1
Oleo-disaturated	5.9
Linoleo-disaturated	7.3
Oleo-linoleo-saturated	40.6
Saturated-dilinoleo	17.8
Oleo-dilinoleo	28.3

[a] T. P. Hilditch and L. Maddison, *J. Soc. Chem. Ind.*, *59*, 162–168 (1940).

The A.O.C.S. recommended standard for refined cottonseed oil[41] is as follows:

Specific gravity at 25°/25°C............................0.916–0.918
Refractive index at 25°C................................1.468–1.472
Iodine value...106–113
Saponification value...................................190–198
Unsaponifiable matter, %...............................Not over 1.5
Titer, °C..32–36
Free fatty acids (as oleic), %.........................Not over 0.25
Clarity..Clear at 70°F. for at least 3 hours

South Texas oils may have an iodine value as low as 99, a titer as low as 30°C., and may not pass the clarity test, due to the separation of solid glycerides.

Cottonseed oil is somewhat remarkable for the amount and variety of nonoil substances in the crude oil. The content of nonglyceride substances, exclusive of free fatty acids, commonly amounts to 2% or more. The following were found by Jamieson and Baughman[43] to be constitutents of the crude oil: raffinose, pentosans, resins, proteoses, peptones, phosphatides, phytosterols, phytosteroline, inosite phosphates, xanthophyll, chlorophyll, mucilaginous substances, and free fatty acids.

Cottonseed oil is readily detected in admixture with other oils, even in small amounts, by the well-known Halphen color reaction.[44] However, the Halphen reaction is destroyed by hydrogenation. From the standpoint of its fatty acid composition, cottonseed oil is distinguished by a combination of high saturated acid content with a relatively high iodine value.

2. Peanut Oil

Peanut oil, from the plant *Arachis hypogaea*, otherwise known as arachis oil, groundnut oil, or earthnut oil, has a rather light yellow color in the crude form, and the characteristic odor and flavor of peanuts. As compared with other seed oils, and particularly cottonseed oil, it is relatively free of phosphatides and other nonoil constituents. The oil sold upon the market in the United States usually contains between 0.5 and 1.0% of free fatty acids, but may occasionally be much higher in acidity.

Jamieson and Baughman[45] found the oil from a number of samples of Spanish-type peanuts grown in the United States to have an average iodine value of 93.7. This appears to be very slightly lower than the average value for oil from the Spanish and Runner varieties cultivated for oil production in this country. According to these authors, large kerneled peanuts of the Virginia type, which are principally grown for other uses in the United States, but which are raised for oil in Africa, China, India, etc.,

[43] G. S. Jamieson and W. F. Baughman, *J. Oil & Fat Ind., 3*, 347–355 (1926).
[44] American Oil Chemists' Society, *Official and Tentative Methods*, 2nd ed., 1946 (revised annually), Official Method Cb 1–25.
[45] G. S. Jamieson and W. F. Baughman, *Cotton Oil Press, 6*, No. 1, 34–35 (1922).

produce an oil of approximately the same iodine value as Spanish peanuts, but with a somewhat different fatty acid composition. The average saturated acid content of Spanish-type peanut oil is about 19 to 20%. Oil from the large kerneled variety usually contains 15 to 17% saturated acids.

Average characteristics of the refined peanut oil produced in the United States are approximately as follows: iodine value, 95; refractive index at 60°C., 1.4558; saponification value, 189; density at 60°C., 0.888; unsaponifiable matter, 0.5%; titer 30°C.

The average peanut oil with the above characteristics will contain about 20% saturated acids, 50% oleic acid, and 30% linoleic acid.

The A.O.C.S. recommended standard for peanut oil is as follows:[46]

Specific gravity at 25°C./25°C. 0.910–0.915
Refractive index at 25°C. 1.467–1.470
Iodine value. 84–100
Saponification value. 188–195
Unsaponifiable matter, %. . . . . Not over 1.0
Titer, °C. 26–32

TABLE 46

CHARACTERISTICS AND COMPOSITION OF PEANUT OIL[a,b]

Iodine value.	93.3
Saponification equivalent.	295.5
Saponification value.	190
Titer, °C.	31.8
Unsaponifiable matter, %.	0.4
Fatty acids (wt. %)	
Palmitic.	8.3
Stearic.	3.1
Arachidic.	2.4
Behenic.	3.1
Lignoceric.	1.1
Oleic.	56.0
Linoleic.	26.0
Glycerides (mol %)	
Mono-oleo-disaturated.	1
Monosaturated-diolein.	11
Saturated-oleo-linolein.	45
Linoleo-diolein.	24
Triolein.	19

[a] T. P. Hilditch, M. B. Ichaporia, and H. Jasperson, *J. Soc. Chem. Ind.*, *57*, 363–368T (1938). B. G. Gunde and T. P. Hilditch, *ibid.*, *59*, 47–53 (1940).

[b] A later analysis of this oil by T. P. Hilditch and J. P. Riley, *ibid.*, *64*, 204–207 (1945), following a slightly different and improved technique, revealed the presence of 0.5% myristic acid (included with palmitic above), and 1.7% hexadecenoic acid (included with oleic above).

[46] See *Oil & Soap*, *18*, 194 (1941).

The detailed analysis of a sample of peanut oil is shown in Table 46. The presence of traces of capric and lauric acids in peanut oil has been reported.[47]

There are no color tests for peanut oil, hence it is most readily detected in other oils through its unusually high content of arachidic, behenic, and lignoceric acids. Various tests based on the presence of these high molecular weight acids are described in the literature.[1b] While these tests serve to indicate qualitatively the presence of considerable amounts of peanut oil in other oils, they do not enable the analyst to detect the presence of minor proportions of other oils in peanut oil, or to estimate with accuracy the relative proportions of peanut oil and other oils in mixtures.[48]

Peanut oil, like cottonseed oil, will solidify if exposed to refrigerator temperatures for an extended time. The cloud and pour points of a typical peanut oil by the A.S.T.M. method are approximately 40° and 34°F.[40]

3. Olive Oil

Olive oil (*Olea europea*) has a greenish yellow color, and a characteristic mild, pleasant flavor and odor. Unlike other vegetable oils, it is consumed as a food without refining, deodorization, or other processing treatment, although oil of poor quality is sometimes refined and blended with a better oil. Since olive oil is more expensive than other vegetable oils it may on occasion be adulterated with the latter. Methods for the detection of various other oils in olive oil will be mentioned under the heading of the individual oils. If present in quantity in other vegetable oils, olive oil may be detected through its high content of squalene.[49]

Oil which has been extracted from olive press cake by solvents is likewise considered an adulterant in edible oils. The detection of extracted and refined oils is discussed at length by Jamieson.[1b]

Characteristics and compositions of a number of samples of olive oil from different sources are shown in Table 47. It is evident that the proportions of the different fatty acids in olive oil may vary considerably, even in oils with very nearly equal iodine values. Iodine values as low as about 75 and as high as about 95 have been reported. Like most other vegetable oils, olive oil tends to become more unsaturated as the climate becomes colder, and the unsaturation of the oil also increases with advancing maturity of the fruit.

The free fatty acid content of olive oil is extremely variable. Some of the better oil contains not more than 0.5–1.5% of free acids, but oil with a free fatty acid content up to 5% or higher is not uncommon. There is a

[47] H. L. Wikoff, J. M. Kaplan and A. L. Berman, *J. Biol. Chem.*, 153, 227–235 (1944).
[48] See S. T. Voorhies and S. T. Bauer, *Oil & Soap*, 20, 175–178 (1943).
[49] J. Fitelson, *J. Assoc. Official Agr. Chem.*, 26, 499–506 (1943).

general relationship between acidity and quality as judged by flavor and odor; oil with a free acid content over about 3% seldom is of really good flavor. Pressing of the oil is commonly carried out in two or more stages, with the first pressing yielding the highest grade, so-called "virgin" oil, and each successive pressing yielding an oil of lower grade. The oils of commerce are commonly blended from a number of stocks of different sources and different grades. The residue from the last expression is solvent extracted, often with carbon disulfide, to produce "sulfur olive oil" or "olive oil foots." This latter product is considered an inedible oil, to be

TABLE 47

COMPOSITION IN PER CENT BY WEIGHT AND CHARACTERISTICS OF OLIVE OIL

Analysis	Cali-fornia[a]	Italy[a]	Spain[a]	Tunisia[a]	Pales-tine[b]	Italy[c]
Iodine value	85.1	84.4	83.7	86.0	84.0	84.2
Refractive index at 20°C	1.4690	1.4690	1.4689	1.4700	—	—
Saponification value	190.6	190.6	192.4	193.6	191	194
Specific gravity at 25°/-25°C	0.9119	0.9120	0.9116	0.9131	—	—
Unsaponifiable matter, %	1.0	1.1	0.8	0.8	1.1	1.3
Acid value	1.5	1.8	1.8	1.9	—	—
Fatty acids, wt. %						
Myristic	Trace	Trace	Trace	0.1	0.5	1.2
Palmitic	6.9	9.2	9.4	14.4	10.0	15.6
Stearic	2.3	2.0	1.4	2.4	3.3	2.0
Arachidic	0.1	0.2	0.2	0.3	0.1	—
Hexadecenoic	—	—	—	—	—	1.6
Oleic	84.4	83.1	80.5	69.1	77.5	64.6
Linoleic	4.6	3.9	6.9	12.0	8.6	15.0
Glycerides (probable composition, mole %)						
Monosaturated-diolein	—	—	—	—	45.3	57.2
Monosaturated-oleolinolein	—	—	—	—	—	4.2
Linoleo-diolein	—	—	—	—	25.5	34.0
Triolein	—	—	—	—	29.2	4.6

[a] G. S. Jamieson, *Oil & Fat Industries*, *4*, 63, 426 (1927).
[b] T. P. Hilditch and H. M. Thompson, *J. Soc. Chem. Ind.*, *56*, 434–438 (1937).
[c] T. P. Hilditch and L. Maddison, *J. Soc. Chem. Ind.*, *60*, 258–262 (1941).

denatured and sold for the manufacture of soap, and for other industrial purposes. However, much of the better extracted oil, including oil from the olive kernels (similar in composition to the pulp oil), undoubtedly finds its way into edible products, after suitable processing treatment.

Olive oil is distinctive among vegetable oils for its low iodine value combined with the property of remaining liquid at low temperatures (down to about 0°C.). In this respect, however, it is closely imitated by teaseed oil. Due to its low content of linoleic acid, it is more stable toward oxidation than most liquid oils; it is almost completely lacking in drying properties, or any tendency to become gummy when exposed in films. Cloud and pour points of a representative olive oil (A.S.T.M. method) are about 22° and 14°F., respectively.[40]

Standards recommended by the A.O.C.S. for edible and inedible olive oils are as follows:[50]

Characteristic	Edible	Olive oil foots[b]
Specific gravity at 25°/25° C.	0.909–0.915	—
Iodine value[a]	80–88	77–90
Saponification value	188–196	186–196
Titer, °C.	17–26	16–26
Crismer test, °C.	68.5–71.6	—
Unsaponifiable matter, %	Not over 1.4	Not over 2.3
Free fatty acids, %	Not over 1.5	—

[a] Minimum I.V. for California oils shall be 79; maximum I.V. for African and Dalmatian oils shall be 92.

[b] Olive oil foots shall contain not over 3% moisture and insoluble impurities, and not over 0.20% ash.

4. Palm Oil

Palm fruits, from the oil palm, *Elaeis guineensis*, are unavoidably subjected to strong enzyme action during their harvesting and handling prior to expression of the oil; consequently even the better grades of oil are much higher in free fatty acids than most seed oils. Oils processed by crude native methods may be hydrolyzed to an extreme degree. The value of the oil bears an inverse relation, of course, to its content of free acids.

Oils are commercially classified and quoted on the basis of their geographical origin and the free fatty acid content characteristic of oils from each particular locality. Sumatran or Malayan plantation oils are the highest grade oils; they are sold on the basis of a 5% content of free fatty acids, calculated as oleic acid. They may contain as little as 3% of free acids. Congo plantation oils are sold on the basis of their containing 10% of free acids. African palm oils obtained from wild trees are classified as "soft," "semisoft," or "hard." Soft oils are quoted on the basis of a 12% free fatty acid content, semisoft or mixed oils are quoted on the basis of 35% free acids, and hard oils on the basis of 45% or more.

Palm oil is colored a deep orange red by the large amount of carotene which it contains (0.05–0.20%). The color is not much affected by re-

[50] See *Oil & Soap*, *13*, 264 (1936).

fining, but palm oil is bleached to a yellow color similar to that of other vegetable oils by hydrogenation. It is also bleached by high-temperature treatment with fuller's earth, by deodorization or other high-temperature treatment, or by oxidation, either by air or chemical means. It has a pleasant, characteristic odor, is very stable toward oxidation, and has no drying properties. At ordinary temperatures of 70° to 80°F. it is semisolid. Its consistency and melting point depend to a large degree upon its content of free fatty acids, as the free acids are higher in melting point than the glycerides. To the palm oil trade, oils with a relatively low free acid content are known as soft oils, whereas those with a high acidity are termed hard oils.

TABLE 48

COMPOSITION OF PALM OILS

Analysis	Cape Palmas (native)[a]	Grand Bassa (native)[a]	Belgian Congo (native)[a]	Cameroons (native)[a]	Malaya (plantation)[b]	Congo (plantation)[c]
Iodine value............	60.0	55.6	54.1	53.3	53.8	52.9
Saponification equivalent.	283.8	282.6	280.1	282.5	282.3	280.3
Fatty acids (wt. %)						
Myristic.............	1.6	0.6	1.3	1.1	1.4	2.4
Palmitic............	32.3	37.6	41.4	45.1	40.1	41.6
Stearic..............	5.5	3.7	4.7	4.1	5.5	6.3
Hexadecenoic........	—	1.4	—	0.8	—	1.8
Oleic...............	52.4	50.3	42.9	38.6	42.7	38.0
Linoleic............	8.2	6.4	9.7	10.3	10.3	9.9[d]
Glycerides (probable composition, mol %)						
Tripalmitin..........	2	3	5.5	5	—	5.0[e]
Dipalmitostearin......	1.5	3	1	3.5	—	1.2
Unsaturated-dipalmitin	16.5	31	29.5	43	—	37.2[f]
Unsaturated-palmitostearin............	16	10	13.5	11	—	10.7
Palmitodiunsaturated.	51	41	44.5	31	—	42.8[g]
Triunsaturated	14	12	6	6.5	—	3.1

[a] T. P. Hilditch and L. Maddison, *J. Soc. Chem. Ind.*, *59*, 67–71 (1940).
[b] T. P. Hilditch and E. E. Jones, *ibid.*, *49*, 363–368T (1930); *50*, 171–176T (1931).
[c] T. P. Hilditch, M. L. Meara, and O. A. Roels, *ibid.*, *66*, 284–288 (1947).
[d] Includes 0.4% linolenic acid.
[e] Includes 0.3% myristodipalmitin.
[f] Includes 4.7% unsaturated-myristopalmitin.
[g] Includes 3.4% myristodiunsaturated and 5.7% stearodiunsaturated.

Average characteristics of palm oil from the Netherlands East Indies and Malaya are approximately as follows: iodine value, 53; saponification value, 198; refractive index at 60°C., 1.4510; density at 60°C., 0.884; unsaponifiable matter, 0.4%; titer, 43.5°C. Some of the African palm oil from uncultivated trees may be as high as 60 in iodine value; iodine values below 50 have occasionally been reported.

Following are the A.O.C.S. recommended standards for palm oil:[51]

Specific gravity at 100°F. (37.8°C.)	0.898–0.901
Refractive index at 40°C.	1.453–1.456
Iodine value	44–58
Saponification value	195–205
Unsaponifiable matter, %	Not over 0.8
Titer, °C.	40–47

From the investigations of Hilditch and co-workers,[52] the composition of palm oils from different sources is quite accurately known. A number of analyses are recorded in Table 48.

There are no distinctive color tests for palm oil, hence this oil is somewhat difficult to detect in admixture with hydrogenated fats. However, palm oil or hydrogenated palm oil, generally develops a slight, distinctive violet-like odor after limited oxidation, hence the presence of this oil is often indicated qualitatively by the appearance of such an odor during the course of stability or accelerated oxidation tests.

5. SUNFLOWERSEED OIL

Sunflower oil is derived from seed of the plant *Helianthus annuus*. In the crude form, the oil is light amber in color; the color of the refined oil is a pale yellow, similar to that of many other vegetable seed oils. The crude oil contains some phosphatides and mucilaginous matter, but less than cottonseed or corn oil. Its free fatty acid content is similar to that of most other seed oils, *i.e.*, 0.5% and above. Sunflowerseed oil has a distinctive, not altogether unpleasant odor which is completely removed by steam deodorization.

Average characteristics of refined sunflower oil are approximately as follows: iodine value, 130, refractive index at 60°C., 1.4599; saponification value, 190; density at 60°C., 0.897; titer, 18°C.; unsaponifiable matter, 0.8%.

The A.O.C.S. recommended standard for sunflowerseed oil is as follows:[51]

Specific gravity at 25°/25°C.	0.915–0.919
Refractive index at 25°C.	1.472–1.474
Iodine value	125–136
Saponification value	188–194
Unsaponifiable matter, %	Not over 1.5
Titer, °C.	16–20

[51] See *Oil & Soap*, *20*, 163–164 (1943).
[52] T. P. Hilditch and E. E. Jones, *J. Soc. Chem. Ind.*, *49*, 363–368T (1930); *50*, 171–176T (1931). H. K. Dean and T. P. Hilditch, *ibid.*, *52*, 165–169T (1933). A. Banks, H. K. Dean and T. P. Hilditch, *ibid.*, *55*, 77–82T (1935). T. P. Hilditch and L. Maddison, *ibid.*, *59*, 67–71 (1940). T. P. Hilditch, M. L. Meara, and O. A. Roels, *ibid.*, *66*, 284–288 (1947).

The composition of sunflowerseed oil, as reported by two different groups of analysts, is shown in Table 49. Of these two oils, the sample examined by Jamieson and Baughman was from seed grown in the United States, while that of Barker *et. al.* was from Argentina. Russian and North Ameri-

TABLE 49

CHARACTERISTICS AND COMPOSITION (PER CENT BY WEIGHT) OF SUNFLOWERSEED OIL

Analysis	Jamieson and Baughman[a]	Barker *et al.*[b]
Iodine value....................	130.8	139.3
Saponification value...............	188.0	—
Specific gravity at 25°/25°C........	0.9193	—
Refractive index at 20°C...........	1.4736	—
Unsaponifiable matter, %..........	1.20	—
Fatty acids		
Palmitic......................	3.6	6.4
Stearic.......................	2.9	1.3
Arachidic.....................	0.6	4.0
Behenic......................	—	0.8
Lignoceric....................	0.4	—
Total saturated..................	*7.5*	*12.5*
Oleic........................	34.0	21.3
Linoleic......................	57.5	66.2
Total unsaturated................	*91.5*	*87.5*

[a] G. S. Jamieson and W. F. Baughman, *J. Am. Chem. Soc.*, *44*, 2952–2957 (1922).
[b] C. Barker, A. Crossley, and T. P. Hilditch, *J. Soc. Chem. Ind.*, *69*, 16–20 (1950).

can sunflowerseed oils analyzed by different workers[53,54] have generally been intermediate in iodine value between the two samples of Table 49.

There are no tests for the detection of sunflowerseed oil in other oils.

6. SESAME OIL

Crude sesame oil, which is derived from the plant *Sesamum indicum*, varies from amber to yellow in color. It refines to a pale yellow. Sesame oil is relatively high in unsaponifiable substances, but these consist largely of sterols and other substances which are not removable by refining. It is relatively low in other nonoil materials.

The unsaponifiable fraction of sesame oil contains a class of substances, sesamin, sesamoline, etc.,[55] which give distinctive color reactions (the well-known Baudouin and Villavecchia tests[1b,56]), hence sesame oil is readily

[53] R. T. Milner, J. E. Hubbard, and M. B. Wiele, *Oil & Soap*, *22*, 304–307 (1945).
[54] See T. P. Hilditch, *The Chemical Constitution of Natural Fats*, 2nd ed., Chapman and Hall, London, 1947, p. 160.
[55] See Y. Villavecchia and G. Fabris, *J. Soc. Chem. Ind.*, *13*, 69 (1894). W. Adriani, Z. Untersuch. Lebensm., 56. 187 (1928). J. Böeseken, W. Cohen, and C. Kip., *Rec. trav. chim.*, *55*, 816 (1936).
[56] American Oil Chemists' Society, *Official and Tentative Methods*, 2nd ed., 1946 (revised annually). Official Method Cb 2–40.

detected even in small amounts in other oils, even after hydrogenation. The unusual stability of sesame oil is possibly attributable to the antioxidant effect of some of the same substances.

The free fatty acid content of crude sesame oil expressed from un-damaged seed is the same as that of other common seed oils, *i.e.*, about 0.5–1.0%.

The sesame oils examined by the author have all had iodine values within the range of 109 to 113, although values as low as 103 and as high as 116 have been reported in the literature. Sesame oil does not cloud at temperatures down to 0°C. Average values for other characteristics are approximately as follows: saponification value, 191; refractive index, at 60°C., 1.4582; density at 60°C., 0.892; titer, 23°C.; unsaponifiable matter, 1.2%.

The A.O.C.S. recommended standard for sesame oil is as follows:[46]

Specific gravity at 25°/25°C	0.914–0.919
Refractive index at 25°C	1.470–1.474
Iodine value	103–116
Saponification value	188–195
Unsaponifiable matter, %	Not over 1.8
Titer, °C	20–24

The analyses of sesame oil reported by three different groups of workers are reported in Table 50. The sample of Jamieson and Baughman was from China; that of Hilditch, Ichaporia, and Jasperson was from India, whereas the origin of that of Hilditch and Riley was not stated.

TABLE 50

CHARACTERISTICS AND COMPOSITION (PER CENT BY WEIGHT) OF SESAME OIL

Analysis	J. and B.[a]	H., I., and J.[b]	H. and R.[c]
Iodine value	110.8	109.6	110.6
Saponification value	189.3	190	—
Specific gravity at 25/25° C	0.9187	—	—
Refractive index at 20°C	1.4731	—	—
Fatty acids			
Myristic	—	—	0.1
Palmitic	7.8	9.1	8.2
Stearic	4.7	4.3	3.6
Arachidic	0.4	0.8	1.1
Total saturated	*12.9*	*14.2*	*13.0*
Hexadecenoic	—	—	0.5
Oleic	49.4	45.4	45.3
Linoleic	37.7	40.4	41.2
Total unsaturated	*87.1*	*85.8*	*87.0*

[a] G. S. Jamieson and W. F. Baughman, *J. Am. Chem. Soc.*, **41**, 775–778 (1928).
[b] T. P. Hilditch, M. B. Ichaporia, and H. Jasperson, *J. Soc. Chem. Ind.*, **57**, 363–368 (1938).
[c] T. P. Hilditch and J. P. Riley, *ibid.*, **67**, 204–207 (1945).

7. CORN OIL

Crude corn or maize (*Zea mays*) oil has a dark reddish amber color and after refining is considerably darker in color than most other vegetable oils, It contains relatively large amounts of phosphatides and other nonoil substances (often 2% or more) and its free fatty acid content (usually above 1.5%) is higher than that of other common vegetable seed oils of good quality. The refined oil contains traces of wax, which cause the oil to cloud when cooled to a low temperature unless they are removed by winterization. It has a characteristic sweetish odor reminiscent of corn sugar, which is completely removed by deodorization.

TABLE 51

CHARACTERISTICS AND COMPOSITION (PER CENT BY WEIGHT) OF CORN OIL

Analysis	Jamieson and Baughman[a]	Longenecker[b]	Baur and Brown[c]
Iodine value	117.2	—	127.1
Saponification value	187.3	—	—
Refractive index at 20°C	1.4717	—	—
Specific gravity at 25°/25°C	0.9185	—	—
Unsaponifiable matter, %	1.7	—	—
Fatty acids			
Myristic	—	1.7	0.1
Palmitic	7.8	11.0	8.1
Stearic	3.6	2.9	2.5
Arachidic	0.4	—	—
Lignoceric	0.2	—	—
Hexadecenoic	—	1.6	1.2
Oleic	46.3	48.8	30.1
Linoleic	41.7	34.0	56.3
Satd. and unsatd. acids above C$_{18}$	—	—	1.7

[a] G. S. Jamieson and W. F. Baughman, *J. Am. Chem. Soc.*, *43*, 2696–2702 (1921).
[b] H. E. Longenecker, *J. Biol. Chem.*, *129*, 13–22 (1939). Figures in mol per cent.
[c] F. J. Baur, Jr., and J. B. Brown, *J. Am. Chem. Soc.*, *67*, 1899–1900 (1945).

Jamieson and Baughman[57] found a number of samples of refined corn oil to have the following average characteristics: iodine value, 126.0; saponification value, 190.6; specific gravity, 25°/25°C., 0.9198; refractive index at 20°C., 1.4748; unsaponifiable matter, 1.25%; saturated fatty acids, 9.4%; unsaturated fatty acids, 85.6%. These values appear to be very near the average for American oils. The titer of corn oil averages about 18°C.

The suggested A.O.C.S. standard for corn oil is as follows:[46]

Specific gravity at 25°/25°C	0.915–0.920
Refractive index at 25°C	1.470–1.474
Iodine value	103–128

[57] G. S. Jamieson and W. F. Baughman, *Cotton Oil Press*, *7*, No. 12, 34 (1924).

Saponification value... 187–193
Unsaponifiable matter, %.................................... Not over 2.0
Titer, °C.. 14–20

Compositions reported for three different samples of corn oil are shown in Table 51.

There are no tests for the detection of corn oil in other oils.

8. SAFFLOWER OIL

Safflower oil, from the plant *Carthamus tinctorius*, is among the most unsaturated of all the oleic-linoleic acid oils. The iodine value, like that of other highly unsaturated seed oils, is quite variable according to climatic conditions, but for oils produced in many regions, including the United States, it averages in the neighborhood of 145.

Milner and co-workers[53] found eight samples of North American oils (from Montana) to have the following average characteristics: iodine value, 149.1; refractive index at 25°C., 1.47497; unsaponifiable matter, 0.5%. The average composition, calculated from iodine and thiocyanogen values, was: saturated acids, 5.7%; oleic acid, 16.4%; linoleic acid, 77.9%. The average titer is about 16°C., the saponification value, about 192; and the density at 60°C., about 0.900.

Barker and Hilditch[58] found that an African oil with an iodine value of 142.5 and a saponification equivalent of 293.5 had the following fatty acid composition, in terms of per cent by weight:

Myristic.. Trace
Palmitic.. 6.4
Stearic... 3.1
Arachidic... 0.2
Oleic... 13.4
Linoleic.. 76.9

Although many of the older analyses show the presence of small percentages of linolenic acid in safflower oil, Winter[58a] has stated positively that this acid is absent (see also Milner *et al.*[53]).

9. POPPYSEED OIL

Poppyseed oil, derived from various varieties of *Papaveracae*, has an iodine value (about 130 to 140) in the range of the linolenic acid oils, but appears to contain no appreciable amount of linolenic acid, since it yields no ether-insoluble bromides.

The characteristics and composition of a sample of poppyseed oil examined by Eibner and Wibelitz[59] were as follows: saturated acids, 7.2%; oleic acid, 28.3%; linoleic acid, 58.5%; iodine value, 133.4; saponification

[58] C. Barker and T. P. Hilditch, *J. Soc. Chem. Ind.*, *69*, 15–16 (1950).
[58a] G. Winter, *J. Am. Oil Chem. Soc.*, *27*, 82–84 (1950).
[59] A. Eibner and B. Wibelitz, *Chem. Umschau*, *31*, 109–120, 121–127 (1924).

value, 197.5. Other characteristics of poppyseed oil are approximately as follows: density at 60°C., 0.898; refractive index at 60°C., 1.4604; unsaponifiable matter, 0.5%; titer, 17°C.

There is no method of detecting poppyseed oil in admixture with other oils.

10. Teaseed Oil

Teaseed oil, from the Oriental plant *Thea sasanqua*, which has the appearance in the crude and refined forms of ordinary vegetable seed oils, is remarkable for being the sole oil of present commercial importance with a composition virtually identical with that of olive oil. However, it can be detected in olive oil or other oils in the amount of as little as 5 to 10% by means of the Fitelson test.[60]

The average iodine value of teaseed ail appears to be very close to that of olive oil, *i.e.*, about 85. Other average characteristics are approximately as follows: saponification value, 192; refractive index at 60°C., 1.4545; density at 60°C., 0.887; titer, 22°C.

A sample of teaseed oil with an iodine value of 86.3 examined by Griffiths, Hilditch, and Jones[61] contained the following fatty acids (in per cent): myristic, 0.3; palmitic, 7.6; stearic, 0.8; arachidic, 0.6; oleic, 83.3; and linoleic, 7.4.

11. Kapok Oil

Kapok oil, from the tropical tree *Eriodendron anfractuosum*, is botanically related to cottonseed oil, and gives the Halphen color reaction even more strongly than does cottonseed oil. However, it can be distinguished from cottonseed oil by the test proposed by Besson.[62] In appearance kapok oil is somewhat lighter than cottonseed oil, and its has a somewhat greenish cast. It contains less nonoil materials than cottonseed oil.

The iodine value of kapok oil appears to vary from about 94 to 100. Reported values for other characteristics are as follows[63-65]: saponification value, 191; refractive index at 25°C., 1.4696; unsaponifiable matter, 0.8% to 0.9%; titer, 30.4°C.

The composition of a sample of kapok oil with an iodine value of 96.0 was found by Jamieson and McKinney[64] to be as follows, in terms of

[60] J. Fitelson, *J. Assoc. Official Agr. Chem.*, *19*, 493–497 (1936).

[61] H. N. Griffiths, T. P. Hilditch, and E. C. Jones, *J. Soc. Chem. Ind.*, *53*, 13–21T (1934).

[62] A. A. Besson, *Chem.-Ztg.*, *38*, 982 (1914); *J. Soc. Chem. Ind.*, *34*, 184 (1915).

[63] E. P. Griffing and C. L. Alsberg, *Ind. Eng. Chem.*, *23*, 908–909 (1931).

[64] G. S. Jamieson and R. S. McKinney, *Oil & Soap*, *13*, 233–234 (1936).

[65] V. C. Mehlenbacher, *Oil & Soap*, *14*, 118–119 (1937).

glycerides (including unsaponifiable matter): palmitic, 10.2%; stearic, 8.4%; arachidic, 1.2; lignoceric, 0.04; oleic, 45.2; linoleic, 32.9%; and unsaponifiable, 0.8.

12. Rice Bran Oil

Rice bran (*Oryza sativa*) oil is invariably high in its content of free fatty acids. While the acidity of crude vegetable oils depends in general upon the care exercised in handling the oil-bearing material prior to extraction of the oil, a rather high acidity is probably inherent in this oil, since rice bran contains an unusually active lipase.[66]   Reddi *et al.*[67] found a free fatty acids content as high as 4–6% even in oil which had been promptly extracted from bran freshly removed from the rice, and upon storage of the bran at 25°C. the acidity of the oil rose at the rate of 1% per hour. The oil contains considerable wax, although the amount can be reduced by special extraction methods,[67] and quite a high content of unsaponifiable material. The depth of color of the crude or refined oil varies considerably; poor oils of high acidity may be difficult to refine and bleach to a color acceptable for edible products. An unusual stability, noticeable particularly in the hydrogenated oil, suggests the presence of potent and unusual antioxidants.

For a typical oil produced from rice grown in Texas, Murti and Dollear[68] noted the following characteristics and composition: iodine value, 102.3; saponification value, 187.6; titer, 25.2°C.; refractive index at 25°C., 1.4708; color, Lovibond, 35 Y, 6.5 R; specific gravity, 25°/25°C., 0.9166; hydroxyl number, 5.0; saturated acids, 17.1%; oleic acid, 46.3%; linoleic acid, 33.1%; linolenic acid, 0.8%; unsaponifiable matter, 2.70%. The following detailed analysis was reported by Jamieson[69] for an oil derived from North American-grown rice:

Iodine value	99.9
Saponification value	185.3
Acid value	73.7
Unsaponifiable matter	4.64%
Myristic acid	0.5%
Palmitic acid	11.7%
Stearic acid	1.7%
Arachidic acid	0.5%
Lignoceric acid	0.4%
Oleic acid	39.2%
Linoleic acid	35.1%

[66] C. A. Browne, *J. Am. Chem. Soc.*, **25**, 948–954 (1903).
[67] P. B. V. Reddi, K. S. Murti, and R. O. Feuge, *J. Am. Oil Chem. Soc.*, **25**, 206–211 (1948).
[68] K. S. Murti and F. G. Dollear, *J. Am. Oil Chem. Soc.*, **25**, 211–213 (1948).
[69] G. S. Jamieson, *Oil & Fat Industries*, **3**, 256–261 (1926).

13. GRAIN SORGHUM OIL

Grain sorghum (*Sorghum vulgare*) oil is quite similar to corn oil. However, it averages a little lower in iodine value (*ca.* 115), and contains in the crude form a somewhat larger amount of wax, derived from the relatively larger seed coating area of the smaller grain.

Kummerow[70] has reported the following characteristics and composition for a typical crude (and dewaxed) oil: iodine value, 119.0; saponification value, 181; refractive index at 25°C., 1.4718; free fatty acids, 1.6%; unsaponifiable, 1.88%. Fatty acid composition: myristic, 0.2%; palmitic, 8.3%; stearic, 5.8%; hexadecenoic, 0.1%; oleic, 36.2%; linoleic, 49.4%.

14. OTHER OLEIC-LINOLEIC ACID OILS

Almond (*Prunus amygdalus*) oil has been examined with respect to its fatty acid and glyceride compositions by Gunde and Hilditch,[71] who reported the following: myristic acid, 1.2%; palmitic acid, 4.5%; oleic acid, 77.0%; linoleic acid, 17.3%; monosaturated dioleins, 17%; linoleodioleins, 52%; triolein, 31%. Bush and Lasher[72] found the iodine values of oils from five varieties of almonds to vary from 102.0 to 105.7.

The following composition was reported by Bickford, Mann, and Markley[73] for a sample of *pecan* (*Hicoria pecan*) oil with an iodine value of 104.5: saturated acids, 4.0%; oleic acid, 70.9; linoleic acid, 25.2; unsaponifiable matter, 0.4%.

The following analysis of *apricot* (*Prunus armeniaca*) kernel oil was reported by Jamieson and McKinney[74]: iodine value, 108.7; saponification value, 190.2; saturated acids, 3.6%; oleic acid, 60.6%; linoleic acid, 30.0%. *Peach kernel* (*Prunus persica*) and *plum kernel* (*Prunus domestica*) oils are very similar to apricot kernel oil.

According to Jamieson,[1b] *grapeseed* oil commonly has an iodine value of 130–140, a saponification value of 180–190, and contains 8–12% saturated acids, 25–30% oleic acid, and 60–65% linoleic acid.

G. Erucic Acid Oils

1. RAPESEED OILS

Rapeseed (*Brassica campestris*) oil, which is dark yellow or amber in the crude form, refines to a yellow color similar to that of other seed oils. The crude oil contains considerable quantities of phosphatides and other

[70] F. A. Kummerow, *Oil & Soap*, *23*, 167–170, 273–275 (1946).
[71] B. G. Gunde and T. P. Hilditch, *J. Soc. Chem. Ind.*, *59*, 47–53 (1940).
[72] W. A. Bush and E. A. Lasher, *Ind. Eng. Chem.*, *33*, 1275 (1941).
[73] W. G. Bickford, G. E. Mann, and K. S. Markley, *Oil & Soap*, *20*, 85–89 (1943).
[74] G. S. Jamieson and R. S. McKinney, *Oil & Soap*, *10*, 147–149 (1933).

impurities. The refined oil has a characteristic pungent, mustard-like odor, which is removed by deodorization. However, deodorized rapeseed

TABLE 52

CHARACTERISTICS AND FATTY ACID COMPOSITION (PER CENT BY WEIGHT) OF
RAPESEED OIL AND RELATED OILS[a]

Oil	Rapeseed Indian (Toria)	Rapeseed Indian (Guzerat)	Rapeseed Polish (Danzig)	Rapeseed Argentine	Jamba Rape Indian	Ravison (Black Sea)
Iodine value	102.3	94.2	90.9	104.3	84.3	108.5
Saponification equiv.	321.3	315.2	308.6	318.0	305.6	315.2
Saponification value	175	178	182	177	184	178
Unsaponifiable matter, %	0.9	0.7	1.3	0.7	1.1	0.8
Free fatty acids, %	1.0	7.3	5.5	1.3	8.6	3.5
Fatty acids						
Palmitic	1.9	1.9	2.8	2.6	4.7	4.3
Stearic	3.5	3.0	1.2	1.0	1.1	2.1
Arachidic	0.7	2.4	0.9	0.6	1.7	1.8
Behenic	0.7	1.4	0.6	2.1	1.1	0.5
Lignoceric	0.8	0.8	0.7	0.5	0.7	0.6
Total sat.	7.6	9.5	6.2	6.8	9.3	9.3
Hexadecenoic	1.5	2.6	2.9	0.6	1.6	0.6
Oleic	12.3	16.3	14.2	16.0	24.0	15.5
Eicosenoic	4.8	5.1	3.5	6.0	11.6	4.1
Erucic	47.8	45.0	52.5	47.3	37.4	38.7
Linoleic	15.8	13.4	12.0	12.5	9.1	20.9
Docosadienoic	1.5	0.9	1.1	0.9	0.5	1.0
Linolenic	8.7	7.2	7.6	9.9	6.5	9.9
Total unsatd.	92.4	90.5	93.8	93.2	90.7	90.7

[a] M. N. Baliga and T. P. Hilditch, *J. Soc. Chem. Ind.*, *67*, 258–262 (1948).

oil is somewhat inclined to revert in flavor and acquire an unpleasant taste different from that of the undeodorized oil. The oil, refined or crude, is unusual for containing traces of sulfur compounds.[75] Refined or otherwise processed rapeseed oil is often called colza oil.

The A.O.C.S. standard for rapeseed oil is as follows:[46]

Specific gravity at 25°/25°C	0.906–0.910
Refractive index at 25°C	1.470–1.474
Iodine value	97–108
Saponification value	170–180
Unsaponifiable matter, %	Not over 1.5
Titer, °C	11.5–15.0
Viscosity (Saybolt Universal at 100°C.), seconds	Not less than 210
Flash point, open cup, °F	Not less than 550
Ether-insoluble bromides, %	Not over 4%
Cold test (A.S.T.M.), °F	Not over 10

[75] T. von Fellenberg, *Mitt. Lebensm. Hyg.*, *36*, 355–359 (1945).

Rapeseed oil is distinguished by its low saponification value, high refractive index in relation to the iodine value, low titer, and low solidification or clouding temperature. It is also slightly more viscous than ordinary oils. In admixture with other oils it may be recognized through its high content of erucic acid, which yields a magnesium soap insoluble in 90% alcohol.[76]

The recent analytical data of Baliga and Hilditch[77] on representative samples of oil are given in Table 52. Hilditch and co-workers[78] have presented the following estimate (in mol percentages) for the glyceride composition of an Indian rapeseed oil of iodine value 103.2: saturated-C_{18} unsaturated-C_{22} unsaturated, 17.7; C_{18} unsaturated-C_{22} unsaturated-C_{22} unsaturated, 54.6; C_{18} unsaturated-C_{18} unsaturated-C_{22} unsaturated, 27.7.

2. Other Erucic Acid Oils

Analyses of *Jamba rapeseed* (*Eruca sativa*) and *ravison* (*Brassica campestris*) oils, which are generally similar to rapeseed oil, are presented in Table 52. Modern analyses of *mustardseed* oil, another similar oil, are not available; however, from older analyses[79] of mustardseed oil and rapeseed oil it would appear that the two are virtually identical in composition.

Clopton and Triebold[80] have reported that *fanweedseed* (*Thlaspi arvense*) oil is quite similar to rapeseed oil in composition, containing 49.0% erucic acid in the mixed fatty acids. However, according to Goss and Ruckman,[81] *tumbling mustard seed* (*Sisymbrium altissimum*) yields an oil of quite different composition, with about 35% linolenic acid and only 25% erucic acid. Oil produced commercially from grain screenings containing the above and other weed seeds may be expected to be quite variable in composition, according to the kind and proportions of the different seeds.

H. Linolenic Acid Oils

1. Linseed Oil

Crude linseed (*Linum usitatissimum*) oil has a dark amber color, and a strong, characteristic odor. The odor of linseed oil (and other linolenic

[76] A. W. Thomas and M. Mattikow, *J. Am. Chem. Soc.*, *48*, 968–981 (1926).
[77] M. N. Baliga and T. P. Hilditch, *J. Soc. Chem. Ind.*, *67*, 258–262 (1948).
[78] T. P. Hilditch, P. A. Laurent, and M. L. Meara, *J. Soc. Chem. Ind.*, *66*, 19–22 (1947).
[79] J. J. Sudborough, H. E. Watson, P. R. Ayyar, and N. R. Damle, *J. Indian Inst. Sci.*, *9A*, 25 (1926). T. P. Hilditch, T. Riley and N. L. Vidyarthi, *J. Soc. Chem. Ind.*, *46*, 457–467T (1937). J. J. Sudborough, H. E. Watson, P. R. Ayyar, and V. M. Mascarenhas, *J. Indian Inst. Sci.*, *A9*, 43–51 (1926).
[80] J. R. Clopton and H. O. Triebold, *Ind. Eng. Chem.*, *36*, 218–219 (1944).
[81] W. H. Goss and J. E. Ruckman, *Oil & Soap*, *21*, 234–236 (1944).

acid oils) appears to be associated to some extent with the highly unsaturated acids of the oil; it is inclined to recur after the oil has been steam deodorized; hence, unlike that of the oleic-linoleic acid oils, is not derived solely from volatile impurities in the oil. The color of linseed oil can be reduced to a pale yellow, similar to that of other refined vegetable oils, by suitable refining and bleaching treatment. The free fatty acid content of linseed oil is not different from that of other seed oils of annual plants, *i.e.*, it ranges upward from about 0.5%, according to the treatment accorded the seed after the latter have reached maturity.

The crude oil contains relatively large amounts of phosphatides and mucilaginous materials, which must be separated from the oil before it is utilized in paints or varnishes. As in the case of cottonseed or soybean oils, these materials become insoluble upon hydration. They are completely removed by alkali refining. When the oil is heated rapidly to a high temperature, these materials separate in the form of "break material," which in the case of crude oils amounts to about 0.1–0.5% of the weight of the oil. Refined oils should contain no break material. Refined linseed oil contains traces of waxes, which separate when the oil is chilled to a low temperature, and are removed from "wintered" oil.

The quality of linseed oil for technical purposes (or for use as a drying oil) is dependent largely upon its degree of unsaturation, as indicated by its iodine value. Since this property is quite variable, it is necessary to blend lots of oil from different sources, in order to obtain commercial oils of consistently high iodine value. Although the average Wijs iodine value of linseed oil from Canada, the United States, or Argentina is probably between 180 and 185, occasional lots are produced, under unusual climatic conditions, with iodine values above 200, or as low as 130 to 140.[82] With other factors equal, the colder the climate in which flaxseed is grown, the higher is the iodine value of the oil. The tendency of flax (and other plants) to produce oil of relatively low unsaturation in mild climates has been attributed by Ivanov[83] to the absence of sharp variations in the temperature between the days and nights, but Dillman and Hopper[84] have accumulated evidence which points rather to the mean temperature during the period of seed growth as the determining factor. The latter authors, from a study of seed analyses at many North American stations varying widely in latitude, altitude, and annual precipitation, have also pointed out that a moisture deficiency during the growing season contributes to low iodine values in the oil, and that varying climatic conditions from year to year lead to a lack of uniformity in the oil from

[82] E. P. Painter and L. L. Nesbitt, *Ind. Eng. Chem., Anal. Ed., 15*, 123–128 (1943). E. P. Painter and L. L. Nesbitt, *Oil & Soap, 20*, 208–211 (1943).
[83] S. L. Ivanov, *Allgem. Oel- u. Fett-Ztg., 29*, 149–150 (1932).
[84] A. C. Dillman and T. H. Hopper, *U. S. Dept. Agr. Tech. Bull.* No. 844 (1943).

a given location. Sallans[85] mentions that, of a series of survey samples of Western Canadian seed, the proportion yielding oil of iodine value greater than 190 varied from 4.8% in 1941 to 33.9% in 1943. There are also important differences in the oil from different varieties of flaxseed grown under the same conditions, with small-seeded varieties generally yielding oil of higher iodine value than large-seeded varieties.[84,85]

From a statistical analysis of data on the composition of 148 samples of linseed oil from different locations in the United States and Canada, Painter[86] developed the following equations for estimation of the approximate fatty acid composition from the iodine value:

$$\% \text{ saturated } = -0.103 \text{ I.V.} + 28.9$$
$$\% \text{ oleic } = -0.382 \text{ I.V.} + 91.4$$
$$\% \text{ linolenic } = 0.552 \text{ I.V.} - 49.1$$

The expression for linoleic acid, derived from the above equations,[87] is:

$$\% \text{ linoleic } = -0.067 \text{ I.V.} + 28.8$$

Somewhat similar equations, derived from the analysis of 54 samples of oil from Saskatchewan seed, have been published by Sallans and Sinclair.[88]

The requirements of A.S.T.M. specification D234–48 for linseed oil (raw) are as follows:

Specific gravity at 15.5°/15.5°C.............................. 0.931–0.936
Acid number, maximum.................................... 4.0
Saponification value..................................... 189–195
Unsaponifiable matter, %, maximum........................ 1.50
Iodine value (Wijs), minimum[a].......................... 177
Loss on heating at 105 to 110°C., max., %................. 0.3
Appearance.. Clear and transparent at 65°C.
Color... Not darker than a freshly prepared solution of 1.0 g. of $K_2Cr_2O_7$ in 100 ml. of pure H_2SO_4 (sp. gr. 1.84).
Foots, max., %
   Heated oil... 1.0
   Chilled oil.. 4.0

[a] If linseed oil of the high iodine number type is desired, the minimum iodine number, as specified above, should be changed to 188.0.

[85] H. R. Sallans, *Can. J. Research, F22*, 146–156 (1944).
[86] E. P. Painter, *Oil & Soap, 21*, 343–346 (1944).
[87] P. O. Powers, *Oil & Soap, 22*, 52 (1945).
[88] H. R. Sallans and G. D. Sinclair, *Can. J. Research, F22*, 132–145 (1944).

The refractive index of linseed oil varies with the iodine value; an average value for an oil with an iodine value of 180 is about 1.468 at 60°C. The titer of linseed oil is about 18–20°C.

The composition of samples of linseed oil of different iodine values, according to recent analyses which may be considered trustworthy, are recorded in Table 53.

TABLE 53

COMPOSITION IN PER CENT BY WEIGHT OF NORTH AMERICAN LINSEED OILS OF DIFFERENT IODINE VALUES

Analysis	Painter and Nesbitt[a]	Painter and Nesbitt[a]	Painter and Nesbitt[a]	Rose and Jamieson[b]	Painter and Nesbitt[a]	Painter and Nesbitt[a]
Iodine value	127.8	164.8	176.8	179.8	193.6	202.8
Refractive index at 25°C	—	—	—	1.4784	—	—
Unsaponifiable matter, %	1.34	0.94	0.85	1.11	0.79	0.91
Fatty acids						
Palmitic	—	—	—	6.3	—	—
Stearic	—	—	—	2.5	—	—
Arachidic	—	—	—	0.5	—	—
Lignoceric	—	—	—	0.2	—	—
Total saturated	16.3	11.8	8.9	9.5	10.3	7.3
Oleic	40.5	26.4	25.3	19.0	15.6	14.2
Linoleic	22.7	22.2	19.2	24.1	15.4	16.7
Linolenic	20.5	39.6	46.5	47.4	58.7	61.8

[a] E. P. Painter and L. L. Nesbitt, *Ind. Eng. Chem., Anal. Ed.*, 15, 123–128 (1943).
[b] W. G. Rose and G. S. Jamieson, *Oil & Soap*, 18, 173–176 (1941).

2. SOYBEAN OIL[89]

Crude soybean oil (*Soja max*) of good quality has a light amber color, which upon alkali refining is reduced to the light yellow of most vegetable seed oils. Soybean oil produced from green or immature beans may contain sufficient chlorophyll to have a greenish cast, which, however, is not usually very evident until after the yellow-red pigments of the oil have been reduced by hydrogenation. Oil produced from badly damaged beans may have a dark brown color difficult or impossible to remove fully by refining and bleaching.

The crude oil, and particularly that obtained by solvent extraction, contains relatively large amounts (1.5 to 2.5%) of nonglyceride materials consisting chiefly of phosphatides. However, before it is marketed, the crude oil is usually greatly reduced in phosphatide content by water washing. The free fatty acid content of good crude soybean oil, like that of many other vegetable oils, is slightly in excess of 0.5%.

[89] For detailed data on the composition and characteristics of soybean oil, see K. S. Markley, ed., *Soybeans and Soybean Products*, Interscience, New York, 1950–1951.

Soybean oil has a typical "beany" odor and flavor. Like that of other linolenic acid oils, the odor and flavor of soybean oil is inclined to return after the oil has been rendered completely odorless and flavorless by high-temperature steam deodorization.

The average iodine value of the soybean oil produced in the United States is in the neighborhood of 130, although iodine values as high as 140 and as low as 103 have been reported. Other average characteristics are approximately as follows: saponification value, 192; refractive index at 60°C., 1.4600; density at 60°C., 0.898; unsaponifiable matter, 0.6%; titer, 24°C.

The A.O.C.S. recommended standard for soybean oil is as follows:[90]

Specific gravity at 25°/25°C.	0.917–0.921
Iodine value (Wijs)	120–141
Saponification value	189–195
Unsaponifiable matter, %	Not over 1.5
Refractive index at 25°C.	1.470–1.476

A.S.T.M. specification D124–48 for raw soybean oil (for technical use) calls for, among other things, a minimum iodine value of 131, as maximum acid value of 3.0, and maximum unsaponifiable matter of 1.5%.

Analyses of soybean oil in terms of its component fatty acids are shown in Table 54. The two oils of Dollear *et al.* in this table, of extremely

TABLE 54

COMPOSITION (PER CENT BY WEIGHT) OF SOYBEAN OIL OF DIFFERENT IODINE VALUES

Iodine value	102.9[a]	124.0[a]	130.4[b]	132.6[c]	139.4[a]	151.4[a]
Myristic (and lower)	—	—	0.3	0.4	—	—
Palmitic	—	—	9.8	10.6	—	—
Stearic	—	—	2.4	2.4	—	—
Saturated C_{20} and above	—	—	0.9	2.4	—	—
Total saturated	*12.0*	*13.2*	*13.4*	*15.8*	*11.9*	*13.5*
Unsaturated C_{16} and below	—	—	0.5	1.0	—	—
Oleic	60.0	34.0	28.9	23.5	24.7	11.5
Linoleic	25.0	49.1	50.7	51.2	55.4	63.1
Linolenic	2.9	3.6	6.5	8.5	8.0	12.1
Total unsaturated	*87.9*	*86.7*	*86.6*	*84.2*	*88.1*	*86.7*

[a] F. G. Dollear, P. Krauczunas, and K. S. Markley, *Oil & Soap, 17*, 120–121 (1940).
[b] T. P. Hilditch and H. Jasperson, *J. Soc. Chem. Ind., 58*, 187–189 (1939).
[c] T. P. Hilditch, M. L. Meara, and J. Holmberg, *J. Am. Oil Chem. Soc., 24*, 321–325 (1947).

low and extremely high iodine values may be considered very exceptional, and all analyses except the recent one of Hilditch, Meara, and Holmberg are probably a little low with respect to the content of linolenic acid.

[90] See *Oil & Soap, 17*, 151 (1940).

Recent analyses by spectral means,[91,92] of oils with iodine values in the range 130–134, have generally shown linolenic acid (glyceride) contents in the range of 7 to 9%.

It will be noted that soybean oil is more constant than linseed oil in the saturated acid content; variation in the iodine value reflects chiefly a variation in the relative proportions of oleic and linoleic acids.[93] Scholfield and Bull[94] have presented the following equations for estimation of the approximate fatty acid composition of soybean oil in terms of its iodine value:

$$\% \text{ saturated} = -0.045 \text{ I.V.} + 20.5$$
$$\% \text{ oleic} = -0.792 \text{ I.V.} + 128.3$$
$$\% \text{ linoleic} = 0.669 \text{ I.V.} - 31.9$$
$$\% \text{ linolenic} = 0.170 \text{ I.V.} - 17.0$$

Soybean oil may be detected spectrophotometrically in cottonseed oil or other oils free from trienoic acids through its linolenic acid content.[91]

3. PERILLA OIL

Crude perilla (*Perilla ocymoides*) oil somewhat resembles linseed oil in odor and appearance. However, it is said to yield no break material upon being heated to a high temperature, hence it may be presumed that its content of phosphatides or other nonoil substances is very low. The free fatty acid content of good perilla oil does not appear to be different from that of linseed oil.

The average iodine value of perilla oil is about 195. Reported analyses of this oil indicate that its iodine value may vary less widely than that of linseed oil; thus, for example Jamieson[95] lists a range of iodine values of 185 to 208. Other average characteristics are approximately as follows: saponification value, 192; refractive index at 25°C., 1.481; unsaponifiable matter, 1.0%; density at 15°C., 0.935. The A.S.T.M. specification for raw or refined perilla oil (D125–48) is as follows:

Specific gravity at 15.5°/15.5°C., Min.	0.932
Saponification value, minimum	190
Iodine value (Wijs), minimum	196
Unsaponifiable matter, %, maximum	1.5
Acid value, maximum	5.0
Loss on heating at 105°C., %, maximum	0.3

[91] R. T. O'Connor, D. C. Heinzelman, and F. C. Dollear, *Oil & Soap*, 22, 257–263 (1945).

[92] T. P. Hilditch and R. K. Shrivastava, *Analyst*, 72, 527–531 (1947).

[93] F. G. Dollear, P. Krauczunas, and K. S. Markley, *Oil & Soap*, 17, 120–121 (1940).

[94] C. R. Scholfield and W. C. Bull, *Oil & Soap*, 21, 87–89 (1944).

[95] G. S. Jamieson, *Vegetable Fats and Oils*, 2nd ed., Reinhold, New York, 1943.

Appearance ....Clear and transparent at 65°C.
Color ....Not darker than a freshly pre-
                                                         pared solution of 1.0 g. of
                                                         $K_2Cr_2O_7$ in 100 ml. of pure
                                                         H_2SO_4 (sp. gr. 1.84), or its
                                                         equivalent   in   iron-cobalt
                                                         solution   or   in   Lovibond
                                                         glasses.

Foots, max., % 2.5

Data on the fatty acid composition of perilla oil are scanty and some-
what conflicting. Perhaps the best estimate to date is that of Brice et al.[96]
for an oil of iodine value 207.3, which is as follows: saturated acids,
6.6%; oleic, 13.5%; linoleic, 14.7%; linolenic, 65.2%.

4. HEMPSEED OIL

Hempseed (*Cannabis sativa*) oil, which is seldom seen in the United
States, is said to be somewhat similar in characteristics and general
appearance to linseed oil of low iodine value, except for its rather greenish
color.

The iodine values reported for hempseed oil range from about 150 to
175. Kaufmann and Juschkewitsch[97] have given the following fatty acid
composition for a sample of oil with an iodine value of 167.0: saturated
acids, 10.1%; oleic acid, 12.6%; linoleic acid, 53.0%, linolenic acid,
24.3%. This analysis, made in 1930, and based upon theoretical thio-
cyanogen values, is undoubtedly somewhat in error with respect to the
relative proportions of unsaturated fatty acids.[98]   A recalculation by
Hilditch,[99] using empirical thiocyanogen values, indicates the following
composition: saturated acids, 10.1%; oleic acid, 16%; linoleic acid, 46%;
linolenic acid, 28%. In an oil of iodine value 174.4, Griffiths and Hil-
ditch[100] found that a total of 8.6% saturated acids consisted of palmitic,
5.8%; stearic, 1.7%; arachidic, 1.1%. The titer of hempseed oil is about
16°C.

5. WHEAT GERM OIL

Wheat germ (*Triticum*) oil is important chiefly because of its high
content (0.3–0.5%) of tocopherols (vitamin E). The commercial (crude)
oil is usually somewhat high in free fatty acids and also in unsaponifiable

[96] B. A. Brice, M. L. Swain, B. B. Schaeffer, and W. C. Ault, *Oil & Soap*, **22**,
219–224 (1945).
[97] H. P. Kaufmann and S. Juschkewitsch, *Z. angew. Chem.*, **43**, 90–91 (1930).
[98] See the discussion of the limitations of past and present analytical methods for
determining oil compositions, pages 125–126.
[99] T. P. Hilditch, *The Chemical Constitution of Natural Fats*, 2nd ed., Chapman
& Hall, London, 1947, p. 156.
[100] H. N. Griffiths and T. P. Hilditch, *J. Soc. Chem. Ind.*, **53**, 75–81T (1934).

matter (2–4%). The average iodine value is about 125. Following are analyses with respect to fatty acid composition of a sample of oil examined by Gunstone and Hilditch,[101] and a sample examined by Radlove[102] which had an iodine value of 128.6, a saponification value of 184.0, an unsaponifiable content of 4.0%, a refractive index at 30°C. of 1.4737, and a specific gravity, 25°/25°C., of 0.9268:

Fatty acids, %	Gunstone and Hilditch	Radlove
Palmitic	16.4	15.5
Stearic	5.6	
Oleic	11.5	25.5
Linoleic	57.3	52.6
Linolenic	29.2	6.3

6. RUBBERSEED OIL

The following analyses have been recorded by Gunstone and Hilditch[101] for two samples of rubberseed (*Hevea brasiliensis*) oil, from Ceylon and Nigeria:

Analysis	Ceylon	Nigeria
Iodine value	139.8	141.0
Saponification equivalent	292.3	290.0
Free fatty acids, %	7.4	15.7
Unsaponifiable, %	0.4	0.9
Refractive index at 40°C	1.4694	1.4693
Fatty acids, %		
Palmitic	10.6	8.7
Stearic	12.3	10.2
Arachidic	1.0	1.3
Oleic	17.1	20.2
Linoleic	35.5	38.4
Linolenic	23.5	21.2

7. OTHER LINOLENIC ACID OILS

A sample of Australian *candlenut* or *lumbang* (*Aleurites molucanna*) oil examined by Gunstone and Hilditch[103] was found to have the following composition and characteristics: iodine value, 164.3; saponification value, 190.5; free fatty acids, 0.3%; unsaponifiable, 0.4%; refractive index at 25°C., 1.4771; palmitic acid, 5.5; stearic, 6.7; arachidic, 0.3; oleic, 10.5; linoleic, 48.5; linolenic, 28.5%.

[101] F. D. Gunstone and T. P. Hilditch, *J. Soc. Chem. Ind.*, *65*, 8–13 (1946).
[102] S. B. Radlove, *Oil & Soap*, *22*, 183–184 (1945).
[103] F. D Gunstone and T. P. Hilditch, *J. Soc. Chem. Ind.*, *66*, 205–208 (1947).

Although related botanically to the tung tree, the candlenut tree produces an oil containing no elaeostearic or other conjugated acid.

Baughman and Jamieson[104] recorded the following characteristics for a *chiaseed* (*Salvia hispanica*) oil with an iodine value of 190.0 (Hanus): saponification value, 194.8; unsaponifiable, 0.7%; acid value, 1.4; refractive index at 20°C., 1.4838; specific gravity, 25°/25°C., 0.9358. For an oil with an iodine value of 198.7 (Wijs, 24 hours), and an acid number of 2.0 Palma, Donde, and Lloyd[105] found in addition a cloud point of −13°C., a pour point of −16.5°C., a titer of −14.7°C., and a fatty acid composition as follows: saturated, 8.7%; oleic, 4.3; linoleic, 28.2; linolenic, 58.8.

Cedar nut oil, which is unknown in the United States, but is apparently of some commercial importance in Russia, is reported to have an iodine value ranging from 150 to 160, and to be otherwise similar in characteristics to other drying oils of equivalent unsaturation. In addition to about 8% of saturated acids, it is reported to contain the following unsaturated acids[106]: oleic acid, 32.5 to 35.8%; linoleic acid, 31.1 to 34.2%; linolenic acid, 16.6 to 27.8%.

Analyses of the oils from *English walnuts* (*Juglans regia*) and American *black walnuts* (*Juglans nigra*) as reported respectively by Griffiths and Hilditch[100] and by Jamieson and McKinney[107] are as follows:

	English walnut	Black walnut
Iodine value	155.7	135.1
Saturated acids	8.1	5.8
Oleic acid	19.1	36.6
Linoleic acid	65.9	50.0
Linolenic acid	6.9	7.6

As the above compositions were in each case calculated with the aid of thiocyanogen values and the assumption of a theoretical absorption of thiocyanogen, they cannot be considered highly accurate with respect to percentages of the different unsaturated fatty acids.[98]

It has been very recently recognized that stillingia (*Stillingia sebifera*) oil is apparently unique among linolenic acid oils in containing a minor proportion (*ca.* 5%) of a decadienoic acid with conjugated double bonds in the 2:3 and 4:5 positions.[108] Owing to this unusual circumstance, the fatty acid composition of the oil has not been fully established; however, Hilditch[108] has tentatively estimated that a sample of Chinese oil of 185.4 iodine value (Wijs) and 207.4 saponification value contained about

[104] W. F. Baughman and G. S. Jamieson, *Oil & Fat Industries*, 6, No. 9, 15–17 (1929).

[105] F. Palma, M. Donde, and W. R. Lloyd, *J. Am. Oil Chem. Soc.*, 24, 27–28 (1947).

[106] S. L. Ivanov and S. B. Resnikova, *Schriften zentral. Biochem. Forsch.-Inst. Nahr.- u. Genussmittelind. U. S. S. R.*, 3, 239–245 (1933).

[107] G. S. Jamieson and R. S. McKinney, *Oil & Soap*, 13, 202 (1936).

[108] T. P. Hilditch, *J. Oil Colour Chem. Assoc.*, 32, 5–21 (1949).

9% saturated acids, 10% oleic acid, 30% linoleic acid, 45% linolenic acid, and 5% of the aforementioned short chain conjugated acid.

Although formerly considered oleic-linoleic acid oils, it has been shown recently by Dunn et al.[108a] that the oils from the seed of citrus fruits contain an appreciable amount of linolenic acid. Two samples of West Indian grapefruit (*Citrus paradisi*) seed oil contained *ca.* 33% saturated acids, 23% oleic acid, 38% linoleic acid, and 6% linolenic acid. A sample of orangeseed oil was very similar in composition; a sample of limeseed oil contained 13% linolenic acid and less oleic acid.

I. Conjugated Acid Oils

A word of explanation is in order regarding the iodine value of conjugated acid oils. Whereas in the case of the oils discussed previously the iodine value is generally the characteristic of paramount importance, it is of only minor significance in oils containing conjugated fatty acids. The reason for this is twofold. In the first place, conjugated acids do not absorb halogens quantitatively; the iodine value of these oils has no absolute theoretical significance. It varies according to the conditions under which the test is made, and is always less than that of nonconjugated oils with the same number of double bonds. In the second place, the drying properties of these oils are of first importance, and even if it were possible to cause the oils to absorb the theoretical quantity of iodine, or a specific fraction thereof, the iodine value would not necessarily measure these properties accurately, since the latter are much more dependent upon the amount of conjugation in the oil than upon the unsaturation of the oil as such.

The quality of a conjugated acid oil is primarily determined by the actual quantity of conjugated acids which it contains; the latter is indicated more nearly by the gelation time of the oil in the Browne or Worstall heat tests[1b] than by any other simple analytical method.

1. Tung Oil

Tung (*Aleurites fordii, montana*) oil (China wood oil) is relatively light in color and relatively free of phosphatides, mucilaginous matter, or other "break material." Since ordinary liquid or "alpha" elaeostearic acid may be rather easily isomerized to a solid "beta" form, tung oil may on occasion contain a precipitate of solid glycerides, or may even completely solidify. Isomerization is produced by exposure of the oil to light or to compounds of sulfur, selenium, etc., and also occurs in oil which has

[108a] H. C. Dunn, T. P. Hilditch, and J. P. Riley, *J. Soc. Chem. Ind.*, *67*, 199–203 (1948).

been obtained from tung kernels by solvent extraction. It may be permanently prevented by heating the oil to 200°C. for 30 minutes.[109]

A.S.T.M. Specification D 12–48 for raw tung oil is as follows:

Specific gravity at 15.5°/15.5°C............................ 0.9400–0.9430[a]
Acid number, maximum[b]................................ 8
Saponification value.................................... 189–195
Unsaponifiable matter, %, maximum..................... 0.75
Iodine value (Wijs), minimum............................ 163
Refractive index at 25°C................................ 1.5165–1.5200
Heat test (A.S.T.M.), minutes, maximum................. 12

Appearance ....Clear and transparent at 65°C.
Color ....Not darker than a freshly prepared solution of 1.0 g.
                           of $K_2Cr_2O_7$ in 100 ml. of pure H_2SO_4 (sp. gr. 1.84), or
                           its equivalent in iron-cobalt solution or in Lovibond
                           glasses.

[a] For American grown tung oil, the minimum specific gravity may be as low as 0.938.
[b] If tung oil of low acid number and pale color is desired, the maximum acid number shall be reduced to 3.0, and the maximum color to 0.03 g. of $K_2Cr_2O_7$ per 100 ml. of H_2SO_4, or its equivalent.

American tung oil of good quality will usually have an acid value well under 1.0, and will gel in the Browne heat test in 9 to 10 minutes. Adulterated tung oil will require longer to gel (10% of soybean oil or other nonconjugated acid oil is said to increase the gelation time in the Browne test 2.5 to 3 minutes) and will yield a sticky, rather than a dry, crumbly gel in the A.S.T.M. heat test.

Diene value determinations are recommended by McKinney, Halbrook, and Rose[110] as a means of detecting adulteration in tung oil. Pure tung oil has a maleic anhydride value by the Ellis-Jones method of about 67 to 71, whereas the admixture of 10% of linseed oil with a tung oil lowered the maleic anhydride value from 70.6 to 63.8, and 20% of linseed oil reduced the maleic anhydride value to 56.8. The refractive index of tung oil, it may be observed, is much higher than that of any of the nonconjugated acid oils. There is an even more marked difference in the dispersion, or variation in the refractive index according to the wave length of the light, and Holmes and Pack[111] have pointed out that this easily determined characteristic will also serve to detect adulteration. Where suitable spectrophotometric equipment is available, it may be used to determine directly the content of elaeostearic acid in the oil and the proportions of the "alpha" and "beta" isomers.[112]

[109] W. G. Rose, A. F. Freeman, and R. S. McKinney, *Ind. Eng. Chem.*, *34*, 612–614 (1942).

[110] R. S. McKinney, N. J. Halbrook, and W. G. Rose, *Oil & Soap*, *19*, 141–143 (1942).

[111] R. L. Holmes and F. C. Pack, *J. Am. Oil Chem. Soc.*, *25*, 163–167 (1948).

[112] R. T. O'Connor, D. C. Heinzelman, R. S. McKinney, and F. C. Pack, *J. Am. Oil Chem. Soc.*, *24*, 212–216 (1947); *Ind. Eng. Chem., Anal. Ed.*, *17*, 467–470 (1945).

The following analyses of relatively old samples of Chinese and American tung oils have recently been published by Hilditch and Riley:[113]

Analysis	Chinese	American
Iodine value (Wijs)	162.6	163.0
Iodine value (Toms)	231.6	218.9
Saponification equivalent	288.7	286.7
Free fatty acids, %	4.1	0.07
Unsaponifiable, %	0.6	0.3
Refractive index at 40°C	1.5120	1.5133
Saturated acids (largely palmitic), %	3.7	5.5
Oleic acid, %	8.8	4.0
Linoleic acid, %	10.5	8.7
Elaeostearic acid, %	77.0	81.8

Apparently no linolenic acid is present.

There is an apparent decrease in elaeostearic acid with age, presumably from polymerization. Careful spectral analyses by O'Connor and co-workers[112] have revealed 82.0–83.5% elaeostearic acid in freshly pressed American oils, which corresponds to 86–88% in the mixed fatty acids. From diene value determinations McKinney and Jamieson[114] estimated that a sample of American oil contained 90.7% elaeostearic acid (in the mixed acids), together with 4.6% saturated acids, 4.1% oleic, and 0.6% linoleic. The freshly expressed oil contains none of the solid "beta" isomer, but the content of this isomer may be considerable (50% or more) in solvent-extracted oil or in old oil, particularly if it has been exposed to light.[112]

2. OITICICA OIL

Oiticica (*Licania rigida*) oil is quite similar to tung oil in most respects. However, it dries less strongly; the heat-treated oil on the North American market is said to have a Browne heat test of about 16 minutes, as compared with about 10 minutes for tung oil. Untreated oil has a slightly longer gelation time (18–24 minutes).

Oiticica oil undergoes isomerization to a solid form even more readily than does tung oil, and formerly much of the oil reaching the United States was thus solidified. The solidified oil may be rendered permanently liquid by heating to above 225°C., and it is the heat-treated oil which is now principally marketed.

The following analysis of raw oiticica oil was reported by McKinney and Jamieson:[115]

[113] T. P. Hilditch and J. P. Riley, *J. Soc. Chem. Ind.*, 65, 74–81 (1946).
[114] R. S. McKinney and G. S. Jamieson, *Oil & Soap*, 15, 30–32 (1938).
[115] R. S. McKinney and G. S. Jamieson, *Oil & Soap*, 13, 10–11 (1936).

Refractive index at 25°C.................................... 1.5145
Saponification value....................................... 192.6
Unsaponifiable matter, %................................... 0.57
Saturated acids, %... 11.3
Oleic acid... 6.2
Licanic acid... 82.5

This analysis may be slightly in error, since it was in part calculated from theoretical thiocyanogen values for oleic and licanic acids.[98] Morrell and Davis[116] reported the presence of a small amount (ca. 5%) of elaeostearic acid in oiticica oil.

A.S.T.M. Specification D601-46 for permanently liquid oiticica oil is as follows:[117]

Specific gravity, 15.5/15.5°C., min........................... 0.978
Viscosity, min., poises....................................... 13
Acid number, max... 8.0
Iodine number, Wijs, min..................................... 135
Color (Gardner 1933), max.................................... 11
Heating test, max., minutes.................................. 17
Refractive index at 25°C., min............................... 1.5100
Matter insoluble in chloroform, max., %...................... 0.1

3. Cacahuanache (Mexican Oiticica) Oil

Cacahuanache or Mexican oiticica (*Licania arborea*) oil appears to be similar to Brazilian oiticica oil in all respects, including the tendency of the latter to isomerize to a solid form after expression. Like oiticica oil it may be rendered permanently liquid by being heated to 225°C. for a short time.

The following characteristics and composition were recently reported for a sample of cacahuanache oil by Rose and Jamieson.[118]

Refractive index at 25°C.................................... 1.5163
Saponification value....................................... 187.3
Iodine value (Wijs one hour)............................... 153.0
Diene value (Ellis-Jones).................................. 60.9
Carbonyl value (Leithe).................................... 121.4
Acid value... 0.8
Unsaponifiable matter, %................................... 0.5
Browne heat test, minutes.................................. 15.5
Saturated acids, %... 11.6
Oleic acid... 5.5
Linoleic acid.. 7.6
Elaeosteric acid... 1.6
Licanic acid... 73.7

[116] R. S. Morrell and W. Davis, *J. Oil Colour Chem. Assoc.*, 19, 359–362 (1936).
[117] See *Oil & Soap*, 19, 140 (1942).
[118] W. G. Rose and G. S. Jamieson, *Oil & Soap*, 20, 227–231 (1943).

J. Marine Oils

The marine oils present unusual difficulties to the analyst because of the wide variety of unsaturated fatty acids that they contain. Whereas ordinary oils may generally be analyzed in terms of the individual acids, in the case of marine oils it is only possible to estimate the various acids according to their chain lengths, and then determine the average degree of unsaturation existing in the unsaturated acids of each different chain length. In the tabulated analyses of these oils in the following section this average degree of unsaturation is expressed in terms of the number of hydrogen atoms lacking to make the acid completely saturated; thus the unsaturation of oleic acid would be expressed as —2.0, that of linoleic acid as —4.0, that of linolenic acid as —6.0, etc. In each case the average degree of unsaturation is placed after the percentage of the fatty acid fraction, in parentheses; thus, for example, the designation 5.9 (—10.1) means that the oil contains 5.9% of the fatty acids in question, and on the average these acids have a deficiency of 10.1 hydrogen atoms, each (equivalent to just slightly over 5 double bonds each).

Because of their content of fatty acids with more than three double bonds, marine oils may be readily recognized when present in other oils by subjecting the mixture to alkali isomerization and ultraviolet spectral examination.[119]

1. Whale Oil

According to Brandt,[120] trading in whale oil is conducted under the following grades:

Grade	Color	Per cent free fatty acids (as oleic)
1..........	Pale straw or yellow	Not over 1
2..........	Amber yellow	1–6
3..........	Pale brown	6–15
4..........	Dark	15–60

In addition to the above, a Grade 0 is also sometimes recognized, consisting of very light colored oil with a free fatty acid content of 0.5% or less. Most of the oil now produced may be classified in the higher grades.

Whale oil varies a great deal in iodine value, but it would appear that most of the oil derived from whales taken in the Antarctic regions ranges between about 110 and 125 in iodine value. Characteristics of whale oil which may be considered somewhat near the average are as follows: iodine value, 120; saponification value, 195; refractive index at 60°C.,

[119] R. S. Lambert and J. T. R. Andrews, *J. Am. Oil Chem. Soc.*, *25*, 414–416 (1948).
[120] K. Brandt, *Whale Oil: An Economic Analysis*, Food Research Institute, Stanford University, 1940.

1.460; density at 60°C., 0.892; unsaponifiable matter, 1.2%; titer, 23°C. The A.O.C.S. recommended standard for whale oil is as follows:[117]

Specific gravity at 25°/25°C.	0.910–0.920
Refractive index at 25°C.	1.470–1.477
Iodine value (Wijs).	110–135
Saponification value.	185–202
Unsaponifiable matter, %.	Not over 2.0

The composition of commercial antarctic whale oil, as reported by Hilditch and Terleski[121] and Hilditch and Maddison[122] is as follows:

Analysis	Hilditch and Terleski[121]	Hilditch and Maddison[122]
Iodine value	109.3	108.0
Saponification equivalent	286.5	287.0
Saturated acids, %		
C_{12}	—	Trace
C_{14}	6.3	9.2
C_{16}	18.2	15.6
C_{18}	2.4	1.9
C_{20}	—	0.6
Total saturated	*26.9*	*27.3*
Unsaturated acids, %		
C_{14}	3.7 (−2.0)	2.5 (−2.0)
C_{16}	13.3 (−2.0)	13.9 (−2.1)
C_{18}	38.4 (−2.6)	37.2 (−2.4)
C_{20}	11.4 (−5.6)	12.0 (−7.1)
C_{22}	6.3 (−9.0)	7.1 (−9.4)
Total unsaturated	*73.1*	*72.7*

2. CALIFORNIA SARDINE OR PILCHARD OIL

Oil derived from the fish *Sardinops caerulea* is known in the United States as sardine oil and in Canada as pilchard oil. Japanese sardine oil is obtained from a different species, *Clupanodon melanostica*.

Sardine oil, like other fish oils, is somewhat inferior in general quality to whale oil, since it is rendered from the whole fish rather than from selected fatty tissues, and hence contains relatively large amounts of protein decomposition products and other nonfat materials. The free fatty acid content of fish oils is also generally somewhat higher than is that of whale oil of good quality.

From the data of Brocklesby[123] it would appear that sardine oil is con-

[121] T. P. Hilditch and J. T. Terleski, *J. Soc. Chem. Ind.*, 56, 315–322T (1937).
[122] T. P. Hilditch and L. Maddison, *ibid.*, 61, 169–173 (1942); 67, 253–257 (1948).
[123] H. N. Brocklesby, *The Chemistry and Technology of Marine Animal Oils*. Fisheries Research Board of Canada, Ottawa, 1941.

sistently higher in iodine value than pilchard oil, average values for the two oils being about 185 and 178, respectively. Iodine values below 170 or above 190 are not often observed, in the case of either oil. Other average characteristics of sardine oil are approximately as follows: saponification value, 191; refractive index at 60°C., 1.4660; density at 60°C., 0.905; unsaponifiable matter, 1.0%; titer, 30°C.

The composition of pilchard (sardine) oil has been reported by Brocklesby and Harding[124] to be as follows:

Saturated acids
C_{14}.. 5.1%
C_{16}.. 14.6
C_{18}.. 3.2
Unsaturated acids
C_{14}.. Trace
C_{16}.. 11.8 (−2.0)
C_{18}.. 17.8 (−3.3)
C_{20}.. 18.1 (−4.1)
C_{22}.. 14.0 (−8.5)
C_{24}.. 15.4 (−10.9)

3. Japanese Sardine Oil

Oil from the Japanese sardine, *Clupanodon melanostica*, appears to differ from American sardine oil in having no appreciable content of C_{24} acids, although its iodine value is about the same as that of the American oil. The iodine values for Japanese sardine oil vary from about 160 to 190.

The following composition was given for Japanese sardine oil by Armstrong and Allan:[125]

Saturated acids
C_{14}.. 5.8%
C_{16}.. 9.7
C_{18}.. 2.3
Unsaturated acids
C_{16}.. 13.0 (−2)
C_{18}.. 14.2 (−2)
C_{18}.. 10.0 (−4)
C_{18}.. Trace (−6)
C_{20}.. 26.0 (−5)
C_{22}.. 19.0 (−5)

The titer of Japanese sardine oil averages about 28°C.

[124] H. N. Brocklesby and K. F. Harding, *J. Fisheries Research Board. Can., 4,* 59–62 (1938).
[125] E. F. Armstrong and J. Allan, *J. Soc. Chem. Ind., 43,* 207–218T (1924).

4. MENHADEN OIL

Menhaden (*Brevoortia tyrannus*) oil appears to vary in iodine value and composition somewhat more than sardine oil, iodine values from about 150 to 185 having been reported. However, the average iodine value of this oil is probably about 170. Other average characteristics of menhaden oil are approximately as follows: saponification value, 191; refractive index at 60°C., 1.4645; density at 60°C., 0.903; unsaponifiable matter, 1.0%; titer, 32°C.

The composition of the mixed fatty acids of menhaden oil, as reported in 1924 by Armstrong and Allan,[125] and more recently by Smith and Brown,[126] is as follows:

Analysis	Armstrong and Allan	Smith and Brown
Saturated acids, %		
C_{12}	—	Trace
C_{14}	5.9	6.8
C_{16}	16.3	15.5
C_{18}	0.6	3.1
C_{20}	0.6	—
C_{22}	0.8	—
Total saturated	24.2	25.4
Unsaturated acids, %		
C_{14}	—	0.1 (−2.0)
C_{16}	15.5 (−3)	14.9 (−2.1)
C_{18}	29.6 (−4)	23.7 (−3.3)
C_{20}	19.0 (−10)	17.5
C_{22}	11.7 (−10)	10.8
C_{24}	—	4.0
C_{26}	—	1.2
Over C_{26}	—	2.4
Total unsaturated	75.8	74.6

The oil examined by Smith and Brown had an iodine value of 182.8 and a saponification value of 191.4.

5. HERRING OIL

Herring (*Clupea harengus*) oil varies extremely in composition according to the season, iodine values of 115 to 144 having been observed by Lovern[127] in fish taken from the same waters at different times of the year. However, the iodine vlaue of commercial oil may be said to average about 140. Other average characteristics are approximately as fol-

[126] F. A. Smith and J. B. Brown, *Oil & Soap*, 22, 277–283, 321–325 (1945); 23, 9–10 (1946).

[127] J. A. Lovern, *Biochem. J.*, 32, 676–680 (1938).

lows: saponification value, 192; refractive index at 60°C., 1.4610; density at 60°C., 0.900; titer, 25°C.

The oil differs from most fish oils in having an unusually high content of unsaturated C_{22} acids and an unusually low content of unsaturated C_{16} acids, combined with unusually high unsaturation in the C_{16} and C_{18} acids and unusually low unsaturation in the C_{20} and C_{22} acids. The differences apply actually to the body fat, and not the visceral fat[128] (Table 55), and are attributed to the peculiar feeding habits of the herring.[127] Although the C_{20} and C_{22} acids have a relatively low average unsaturation, this arises principally from the occurrence of a high proportion of monoethenoid acids in this class of acids, which nevertheless includes considerable amounts of pentaethenoid, and even hexaethenoid acids.[129]

The characteristics and compositions noted by different groups of observers are listed in Table 55.

Bjarnason and Meara[129] estimate the glycerides of an oil of 140 iodine value are 4% disaturated, 61% monosaturated, and 35% triunsaturated.

TABLE 55

CHARACTERISTICS AND COMPOSITION (PER CENT BY WEIGHT) OF HERRING OIL

Analysis	Lovern[a]	Bjarnason and Meara[b]	Hilditch and Pathak[c] (visceral fat)
Iodine value	138.6	140.0	146.8
Saponification equivalent	—	300.7	296.2
Unsaponifiable, %	—	1.3	0.75
Free fatty acids, %	—	2.6	5.7
Saturated fatty acids, %			
C_{12}	—	0.1	—
C_{14}	7.3	7.0	5.8
C_{16}	13.0	11.7	15.7
C_{18}	Trace	0.8	2.8
C_{20}	—	0.1	0.3
Total saturated	20.3	19.7	24.6
Unsaturated fatty acids, %			
C_{14}	0.8 (−2.0)	1.2 (−2.0)	1.4 (−2.0)
C_{16}	4.9 (−2.7)	11.8 (−2.4)	10.5 (−2.5)
C_{18}	20.7 (−4.2)	19.6 (−3.5)	31.8 (−2.6)
C_{20}	30.1 (−4.6)	25.9 (−5.2)	22.4 (−7.1)
C_{22}	23.2 (−4.3)	21.6 (−4.3)	9.3 (−10.5)
C_{24}	—	0.1 (−3.8)	—
Total unsaturated	79.7	80.2	75.4

[a] J. A. Lovern, *Biochem. J.*, *32*, 676–680 (1938).
[b] O. B. Bjarnason and M. L. Meara, *J. Soc. Chem. Ind.*, *63*, 61–63 (1944).
[c] T. P. Hilditch and S. P. Pathak, *Biochem. J.*, *42*, 316–320 (1948).

[128] T. P. Hilditch and S. P. Pathak, *Biochem. J.*, *42*, 316–320 (1948).
[129] O. B. Bjarnason and M. L. Meara, *J. Soc. Chem. Ind.*, *63*, 61–63 (1944)

6. Fish Liver Oils

Cod liver oil, from the fish *Gadus morrhua*, the most important of the fish liver oils, varies greatly in iodine value, vitamin potency, and general quality. The higher grades of cod liver oil are used exclusively as medicinal oils; the term "cod oil" refers to a low grade of liver oil, used principally in leather manufacture. Iodine values ranging from about 118 to 186 have been reported for this oil; the average value for commercial oils is probably between 160 and 170. Other average characteristics are approximately as follows: saponification value, 186; density at 25°C., 0.925; refractive index at 25°C., 1.481; unsaponifiable matter, 1.0%; titer, 18°C. The free fatty acid content of medicinal cod liver oil is generally below 0.5%, but that of cod oil may be very high.

Cod liver oil contains less saturated acids than other common marine oils, but its unsaturated acids do not appear to be different from those of most fish body oils. The following analysis, reported by Guha, Hilditch, and Lovern[130] for Newfoundland cod liver oil, is typical:

Iodine value	163.0
Saponification equivalent	301.1
Free fatty acids, %	0.46
Unsaponifiable matter, %	0.87
Saturated acids, %	
C_{14}	5.8
C_{16}	8.4
C_{18}	0.6
Unsaturated acids, %	
C_{14}	0.2
C_{16}	20.0 (−2.3)
C_{18}	29.1 (−2.8)
C_{20}	25.4 (−6.0)
C_{22}	9.6 (−6.9)

In recent years a number of other fish liver oils have attained considerable importance as medicinal oils or sources of vitamin concentrates. These include halibut liver oil, tuna liver oil, dogfish liver oil, the liver oil of the soup fin shark and other sharks, etc. Most of these oils are much richer sources of vitamin A than is cod liver oil. Detailed analyses indicating the compositions of these oils are not generally available.

Analyses of cod liver oil and other fish liver oils for vitamin content are given in Chapter I.

[130] K. D. Guha, T. P. Hilditch, and J. A. Lovern, *Biochem. J.*, *24*, 266–290 (1930).

K. Hydroxy Acid Oils

CASTOR OIL

Castor (*Ricinus communis*) oil is the only commercially important oil containing major amounts of a hydroxy acid. Two grades are recognized by the trade: No. 1, which is obtained by the first cold pressing of the beans, is practically colorless, and suitable for medicinal purposes; and No. 3, which is obtained by further pressing or solvent extraction, is more or less colored, and is used only for industrial purposes.

The A.O.C.S. recommended standard for castor oil is as follows:[46]

Specific gravity at 25°/25°C.	0.945–0.965
Refractive index at 25°C.	1.473–1.477
Iodine value (Wijs).	81–91
Saponification value.	176–187
Unsaponifiable matter, %.	Not over 1.0
Acetyl value (André-Cook).	Not less than 144

The following analysis of a sample of castor oil was reported by Kaufmann and Bornhardt:[131]

Iodine value (Kaufmann).	85.8
Saponification value.	195.4
Saturated acids.	2.4
Dihydroxystearic acid.	0.6
Oleic acid.	7.4
Ricinoleic acid.	87.0
Linoleic acid.	3.1

Castor oil is distinguished from other oils by its high acetyl or hydroxyl value, and from other oils of comparable iodine value by its high specific gravity. Unlike other oils, it is miscible with alcohol, but is only slightly soluble in petroleum ether at room temperatures. It is much more viscous than other oils (see pages 74–77), and when completely hydrogenated has an abnormally high melting point (86–88°C.). The titer of castor oil (*ca.* 3°C.) is lower than that of any other common oil of equivalent unsaturation.

[131] H. P. Kaufmann and H. Bornhardt, *Fette u. Seifen, 46,* 444–446 (1939).

C. INDUSTRIAL UTILIZATION OF FATS
AND OILS

COOKING AND SALAD OILS. SALAD DRESSINGS

A. Introduction

The oil and fat products which are used for edible purposes may be divided into two fairly distinct classes: (1) liquid oils, such as olive oil, and (2) plastic fats, such as butter and lard. In the preparation of some foods it is of no particular consequence whether the fatty material used is liquid or solid, but in certain others the consistency of this material is a matter of great importance. For example, in the preparation of a green salad, the object is to provide an oily coating for the various ingredients of the mixture. For this purpose, a liquid oil must be used; a plastic fat, such as butter or lard is entirely unsuitable. On the other hand, it would be impossible to use a salad oil in the place of a plastic fat in making a pound cake. The leavening of such a cake depends entirely upon the air that can be whipped into the fat contained in it, and air cannot be incorporated into a liquid oil.

For reasons related to both history and climate, there are decided geographical divisions of fat- and oil-consuming peoples. The forebearers of the present inhabitants of central and northern Europe derived their edible fats almost wholly from domestic animals. Consequently, the food habits and cuisine of these people were developed around the use of plastic fats, and butter, margarine, lard, and shortenings continue to be their principal fatty food materials.

On the other hand, in the older civilizations of southern Europe, northern Africa, the Near East, and the Orient, the pressure of population has long since made the extensive raising of livestock impractical, and has required the edible oils of these regions to be derived principally from intensively cultivated vegetable crops. In the more tropical regions of the globe, conditions are relatively unfavorable for livestock production, but are extremely well suited to the culture of certain oil-bearing plants, some of which flourish in the wild state.

Oil-bearing plants all yield liquid oils or oils which like that of the coconut are normally liquid at the temperatures generally prevailing where the plant grows. The native cuisine of peoples accustomed to these oils naturally does not include preparations requiring the use of plastic fats.

191

In the New World, plastic fats are the most widely used edible materials, because of the predominantly northern European extraction of the earlier North American settlers, and the fact that large sections of both North and South America are eminently adapted to the large-scale raising of domestic animals.

There is probably in general a somewhat greater utilization of liquid oils in the countries which largely consume plastic fats than of plastic fats in oil-consuming regions. This is in part due to the relatively greater heterogeneity of the population in some of the former, notably in the United States, and in part to the generally more cosmopolitan cuisine of the more highly industrialized countries.

Liquid oils are in general suitable for all classes of cooking except those which require the production of a highly developed dough structure. They are, of course, unsuitable as spreads for bread or for the production of plastic products such as cream icings or fillings.

In a typical meal prepared with plastic fats, the various meat and vegetable dishes will be relatively low in fat content, and a large part of the total fat in the food will be in the form of butter or margarine, to be spread on bread. In a typical meal containing only liquid oils, there will be no spread for the bread, but the meat and vegetable dishes will be enriched by sauces and gravies of high oil content.

In addition to their household and restaurant uses, cooking oils are in considerable demand for commercial deep frying, particularly for products such as doughnuts, which are consumed reasonably soon after their preparation. For frying potato chips and similar packed products which must be able to withstand considerable periods of storage, plastic, hydrogenated oil products are generally preferred, because of their greater stability.

Cooking oils are also used in some quantity for packing certain canned meat and fish products, including sardines, anchovies, and sausages.

All cooking oils are vegetable products. The only liquid animal oils are of marine origin (chiefly whale and fish oils), and these oils, because of their high degree of unsaturation, are, in most parts of the world, not considered edible in the natural form. They are edible after hydrogenation and deodorization but then are, of course, fats rather than oils.

In the United States there is a rather sharp differentiation between cooking oils and salad oils. The latter term is applied to oils which will remain substantially liquid in a refrigerator at 40° to 45°F., and produce a mayonnaise emulsion which is stable at low temperatures.

The labeling of an oil as a cooking oil implies that it will not withstand low temperatures without congealing. Much the greater part of the finished edible oil sold in the United States is labeled and marketed as salad oil, regardless of its intended use.

Salad and cooking oils are of two different kinds: (*1*) naturally flavored oils, and (*2*) neutral, deodorized products. Olive oil is invariably marketed in the undeodorized form. In olive oil, as in butter, the natural flavor of the product is an important asset. It is principally because of its distinctive and highly prized flavor that olive oil is generally more expensive than other vegetable oils.

The vegetable oils other than olive oil may or may not be processed for flavor removal, depending upon local taste and custom. In the Orient the common cooking oils, such as soybean, peanut, rapeseed, sunflower, and sesame oil are generally consumed in their crude form, as expressed from the oil seeds. In Occidental countries, however, it is the more general practice to subject these oils first to refining and deodorizing treatment.

One reason for the general practice of deodorizing vegetable oils in Europe and North and South America is the relative unfamiliarity of the people of these regions with natural oil flavors. The movement of edible vegetable oils from Africa and Asia to Europe and America has grown to large proportions in the past few decades, but the bulk of this oil has been manufactured into margarine or shortening, rather than consumed in the liquid state. Since oils must be processed for flavor removal before they can be used in either of these products, this movement has done little to accustom Americans and Europeans to the natural taste of the foreign oils.

In the United States, deodorized oils are in particular demand. The only vegetable oil consumed in the United States for many years was cottonseed oil, which is so strongly and unpleasantly flavored that processing treatment is absolutely necessary to render it edible. The wide-scale sale of neutral cottonseed oil products over many years has developed a general preference for odorless and tasteless fats in this country which appears to be growing yearly.

Another reason for the practice of deodorizing edible oils for consumption in European and American countries relates to the different quality of the oil obtained by Oriental and Occidental methods of extraction. In such countries as India and China, edible oils are principally produced in small, relatively crude mills, by expressing the oil seeds at low pressures and without previous heat treatment. A low yield of oil is obtained by such methods, but a minimum amount of nonoil substances is expressed from the seed, and the oil is consequently of relatively mild flavor and odor.

In the industrial nations of the Occident, the extraction of oil from oil seeds is carried out in large factories. These factories handle a great volume of material and operate on a highly competitive basis. Naturally every effort is made to obtain the greatest possible yield of oil from

the oil bearing materials. Very high pressures are used in expressing the oil, and in order to improve the efficiency of extraction the oil seeds are cooked or given a heat treatment before they are pressed. In some cases extraction by means of solvents is substituted for mechanical expression. By such methods the quality of the oil is in no wise impaired, insofar as its stability or its nutritive qualities are concerned, but it has a stronger flavor and odor than oil prepared by low-pressure expression of uncooked seeds. The expense of refining and deodorizing the oil to render it palatable is more than compensated by the greater amount of oil obtained.

The consumption of mayonnaise and salad dressings simulating mayonnaise has increased tremendously in the United States in the past 20 to 30 years, principally because of their widespread adoption as spreads for bread. Vast quantities are now used in sandwich shops, drugstores, and in the home for supplying the fat which is considered essential in the preparation of sandwiches. For commercial use in sandwich making they have, in fact, virtually supplanted butter or margarine. To a commercial sandwich maker they are attractive in a number of different ways. They have considerable flavor of their own, and they readily blend with a minimum amount of other, more expensive ingredients to form an acceptable filling. They are less perishable than butter or margarine, and are much more mobile, and easily handled and spread.

As mayonnaise consists largely of oil, it may be said that its manufacture actually represents a method for converting a liquid oil to a plastic product competitive with butter.

Complete data on the production and consumption of salad and cooking oils and mayonnaise and salad dressings in the United States are not available. Estimates are prepared annually by the U. S. Department of Agriculture on the consumption of edible fats and oils other than butter, lard, shortening, and margarine, however, and these may be taken as very nearly equal to that of salad and cooking oils, as the consumption of other edible fats, such as confectioner's fats, etc., is not large. Estimates for recent years were as follows (in millions of pounds):

Average 1937–1941	950
1944	870
1945	795
1946	864
1947	988
1948	1021

In 1947, U. S. Bureau of the Census reports[1] show 10,777 thousand pounds of peanut oil, 166 thousand pounds of sesame oil, 159,876 thousand pounds of soybean oil, and 348,108 thousand pounds of cottonseed

oil consumed in the manufacture of "other edible products." The 1947 Census of Manufactures shows 646,169 thousand pounds of vegetable oil consumed in the manufacture of salad and cooking oils in establishments engaged primarily in shortening manufacture. In addition, 190,906 thousand pounds of refined corn oil was produced in other establishments, and virtually all of this was doubtless marketed eventually as a salad oil.

Recent wholesale prices of various salad and cooking oils, in comparison with crude oil prices, are shown in Table 56.

The estimated production and value of mayonnaise and salad dressing produced in the United States in 1944 are given in Table 57.

TABLE 56

AVERAGE WHOLESALE PRICES (CENTS PER POUND) ON U. S. MARKETS OF SALAD AND COOKING OILS AND CORRESPONDING CRUDE OILS DURING SPECIFIED YEARS[a]

Oil	Average 1935–1939	1941	1943	1946	1948
Corn, edible, drums, N. Y.	10.8	13.0	16.2	20.1	33.4
Cottonseed, edible, salad, drums, N. Y.	10.9	12.8	16.2	20.3	33.5
Peanut, edible, drums, N. Y.	—	—	16.5	—	33.5
Soybean, edible, drums, N. Y.	—	11.7	14.9	19.0	28.3
Olive oil, imported, edible, drums, N. Y.	26.3	62.5	69.4	—	62.0
Olive oil, California, edible, drums, N. Y.	—	—	62.1	—	58.2
Crude corn, tank cars, mills	8.0	10.0	12.8	15.6	25.7
Crude cottonseed, tank cars, mills	7.6	9.5	12.8	15.8	25.3
Crude peanut, tank cars, mills	8.0	9.7	13.0	15.9	25.8
Crude soybean, tank cars, mills	6.8	8.5	11.8	14.6	22.3

[a] *Agricultural Statistics*, 1946, 1949, U. S. Dept. Agr.

TABLE 57

MAYONNAISE AND SALAD DRESSINGS: ESTIMATED U. S. PRODUCTION AND VALUE TO MANUFACTURER IN 1944[a]

Product	Production, million gals.	Value, dollars per gal.
Mayonnaise	20.3	1.85
Salad dressing	31.5	1.47
Sandwich spreads, salad dressing base	3.8	1.60
French dressing	2.5	1.81
Other dressings	0.6	2.08[b]

[a] S. M. Sackrin, Foodstuffs, Fats, and Oils Division, U. S. Dept. Commerce, *Salad Dressing, Mayonnaise, and Related Products—1945.*
[b] For Thousand Island dressing.

B. Olive and Other Naturally Flavored Oils

The manufacture of olive and other naturally flavored salad and cooking oils requires nothing more than extraction of the oil from the oil-

bearing materials, clarification of the extracted oil by filtration or settling, and packaging of the resultant product.

The more popular brands of olive oil are blends of oil from a number of different sources. The quality and flavor of olive oil varies considerably from one season and one locality to another, and in order to turn out a product of more or less uniform characteristics, it is necessary for the packer to have access to a variety of oils.

There is a considerable sale of "virgin," cold-pressed oils such as peanut, sesame, and sunflowerseed in many European countries, as well as in the Far East, but in the United States the sale of undeodorized vegetable oils other than olive oil is virtually nil.

The annual world consumption of olive oil averages about two billion pounds. There is no way of estimating the quantities of soybean, peanut, palm, coconut, sesame, sunflower, rapeseed, and minor oils which are annually consumed in an unprocessed form in different parts of the world, but the total is undoubtedly large. The consumption of olive oil in the United States has never been great, and has declined since World War II. The largest consumption in recent years was 76.3 million pounds in 1931. In 1948, 36.1 million pounds were imported and consumed. Domestically produced oil amounts usually to 4–6 million pounds per year, and has never exceeded about 12 million pounds (in 1940).

C. Neutral Cooking Oils

Deodorized cooking oils are principally prepared from cottonseed, peanut, sunflower, sesame, corn, soybean, and rapeseed oils. Of these oils, the five first mentioned may be considered the most choice, as all may be converted to bland, neutral products, which do not readily deteriorate in flavor. Soybean oil is subject to a characteristic reversion to a slight "beany" flavor. This flavor is not objectionable to all consumers, but it has the effect, none the less, of somewhat limiting the use of this oil as a salad and cooking oil. Deodorized rapeseed oil also has a characteristic flavor reversion.

The processing treatment required for converting crude oils to neutral cooking oils is relatively simple. The oil is first refined, usually with caustic soda. If the color of the finished oil is not critical, the oil is then deodorized without bleaching. If a very light colored oil is desired, the oil is bleached with fuller's earth before it is deodorized.

There are no available data on the production and consumption of cooking oils, as distinguished from salad oils, in the United States.

D. Neutral Salad Oils

As mentioned previously, most of the neutral oil sold in the United

States is actually salad oil, rather than cooking oil, the difference between the two being that salad oil will not solidify at temperatures of 40° to 50°F., whereas cooking oil may do so. The preference for salad oils in this country is principally due to the widespread use in the home of mechanical refrigerators, which provide a food storage temperature of 40° to 45°F. An oil which becomes solid in the refrigerator is inconvenient to handle, as it will not pour from its container. In addition, a mayonnaise salad dressing made from such an oil and kept in the refrigerator will suffer a breakdown of its emulsion due to crystallization of the oil.

Refined sesame, sunflower, corn, and rapeseed oil all remain liquid naturally at low temperatures, hence in the case of products prepared from these oils there is usually no distinction between salad oils and cooking oils. Cottonseed oil must be subjected to "winterization," for removal of its higher melting glycerides, before it may be classified as a salad oil. Soybean oil, sunflower oil, and corn oil deposit a very small quantity of wax upon chilling, which must be removed if a product is to be obtained which will remain perfectly clear at low temperatures. Peanut oil, because of its tendency to deposit very difficultly filterable crystals, is not winterized commercially, and hence is not marketed as a true salad oil, but only as a cooking oil.

Almost all the corn oil now available is made into a salad or cooking oil. The large use of corn oil for this purpose is partly due to the fact that it requires no winterization, and partly due to its rather dark natural color, which is undesirable in shortening and margarine. The relatively limited use of soybean oil is due to its tendency to revert in flavor. Sunflower oil is an excellent naturally winterized salad oil, but is not normally available in any considerable quantity in the United States.

The procedure followed in manufacturing salad oils does not differ from that employed for making cooking oils except in the case of cottonseed oil, which must be winterized. Winterization is always carried out after refining and bleaching but before deodorization.

The extent to which salad oils are bleached depends to some extent upon the trade for which they are designed. The brands of cottonseed salad oil which are most popular for home use in the United States are quite light, with Lovibond red colors of 1.5 to 2.5 units. However, a certain class of trade, particularly that accustomed to the rather dark color of olive oil, prefers a more strongly colored oil. For this trade, an oil is manufactured with a red color of 4.0 to 6.0 units. Refined, unbleached cottonseed oil becomes considerably lighter with deodorization, and for the production of dark salad oils it may be necessary to refine specially the crude oil with the object of producing an abnormally dark refined oil. For commercial mayonnaise and salad dressing manufacture

TABLE 58

Analyses of Typical Commercial Samples of Salad and Cooking Oils

Analysis	Olive oil	Salad oil (corn oil)	Salad oil (soybean oil)	Salad oil (winterized cottonseed oil)	Salad oil (winterized cottonseed oil)	Cooking o (cottonseed oil)	Cooking oil (peanut oil)
Iodine value	85.0	125.0	132.0	112.0	111.5	108.0	95.0
Refractive index at 60°C	1.4546	1.4598	1.4602	1.4577	1.4576	1.4572	1.4550
Free fatty acids, per cent as oleic	1.5	0.05	0.02	0.02	0.02	0.03	0.03
Smoke point, °F	—	420	450	450	450	440	440
Keeping quality, Swift method, hrs. to, peroxide, value of 125	20	10	8	10	10	10	12
Color, Lovibond	—	35Y–6.0R	15Y–1.8R	15Y–1.5R	35Y–4.5R	20Y–2.5R	15Y–1.5R
Flavor and odor	Characteristic	None	Slightly beany	None	None	None	None
Cold test, hrs. to cloud at 32°F	Over 24	Does not cloud	Does not cloud	14	10	<1	<1
Cloud point, A.S.T.M. °F[a]	22	12	14	24	26	38	40
Solid point, A.S.T.M., °F[a]	14	8	10	20	22	28	34
Titer, °C	23.0	18.5	21.5	33.0	33.2	36.0	31.3

[a] Modified by examination of sample at intervals of 2°F. rather than 5°F.

a dark colored oil is acceptable, as a yellow color is desired in the finished product.

The standard method of evaluating the winterization of salad oils' is the cold test of the American Oil Chemists' Society. The oil sample, in a sealed 4-ounce bottle, is placed in a bath of melting ice at 32°F. If it remains clear at the end of 5.5 hours, it is considered a suitably winterized oil. Most cottonseed salad oils, however, will remain clear for 8 to 16 hours and an exceptionally well winterized oil may have a cold test of 24 hours or longer. From a practical standpoint the number of hours required for the oil to cloud is of less significance than the character and amount of the crystals deposited after a prolonged period of storage, at 32°F., or higher. Some oils may cloud quite readily, yet remain in a fluid condition for an extended period of time. Others may be relatively slow in clouding, but thereafter may quickly become semisolid or solid.

Recently, there has been a considerable use of crystallization inhibitors, such as lecithin, blown (oxidized) oils, etc., for extending the cold test of winterized cottonseed oil.[2]

The pour points and solidifying points of salad oils, as determined by the A.S.T.M. method for mineral oils, are also an indication of the extent to which an oil will withstand low temperatures. Cold tests, pour points, solidifying points, and other analytical data on typical samples of commercial salad oils are given in Table 58.

Manufacturers of mayonnaise and other large users of oils purchase the oil in 55-gallon drums or tank cars. Oil packaged in 1-gallon and 5-gallon cans goes principally to restaurants and hotels. The most popular household packages are 1-quart and 1-pint cans or bottles.

E. Salad Dressings

1. Mayonnaise

(a) *Composition*

According to the definition officially adopted in 1931 by the U. S. Food and Drug Administration, mayonnaise consists of the following:

The semisolid emulsion of edible vegetable oil, egg yolk or whole egg, a vinegar and/or lemon juice, with one or more of the following: salt, other seasoning commonly used in its preparation, sugar, and/or dextrose. The finished product contains not less than 50% of edible vegetable oil.

[2] For information on patented crystallization inhibitors, see the following: D. P. Grettie (to Industrial Patents Corp.), U. S. Pat. 2,050,528 (1936); W. Clayton, S. Back, R. I. Johnson, and J. F. Morse (to Crosse and Blackwell), U. S. Pat. 2,097,720 (1937); E. W. Eckey and E. S. Lutton (to Procter & Gamble Co.), U. S. Pat. 2,266,591 (1944); H. D. Royce (to The Southern Cotton Oil Co.), U. S. Pat. 2,418,668 (1947).

Actually, the ingredients of mayonnaise are almost always cottonseed, soybean or corn oil, vinegar, eggs or yolk, sugar, salt, mustard, and white pepper. Although mayonnaise may legally contain as little as 50% of oil, the usual content is between 70% and 80%. The consistency of the emulsion depends to some extent upon the volume ratio of its aqueous and oil phases, and it is difficult to produce a mayonnaise with a sufficiently stiff body with less than this proportion of oil. Also, the use of a low percentage of oil necessitates the use of a relatively high proportion of egg yolks, which are normally more expensive than the oil. Two typical formulas for mayonnaise are the following (all ingredients in terms of per cent by weight):

Ingredient	Formula A	Formula B
Oil	75.00	80.00
Vinegar (4.5% acetic acid)	10.80	9.40
Egg yolk	9.00	7.00
Sugar	2.50	1.50
Salt	1.50	1.50
Mustard	1.00	0.50
White pepper	0.20	0.10

The color of mayonnaise is a pale creamy yellow. The color derives mainly from the egg yolks used in its manufacture, rather than from the oil.

Physically, mayonnaise consists of an internal, or discontinuous phase of oil droplets dispersed in an external or continuous aqueous phase of vinegar, egg yolk, and other ingredients. The vinegar, sugar, salt, and spices largely determine the flavor of the product. The egg yolks also contribute to the flavor, but their chief function is that of an emulsifying agent.[3]

In making mayonnaise it is generally desired to produce as stiff an emulsion as possible. When mayonnaise is made up according to a given formula, the stiffness of the emulsion is principally determined by the degree of subdivision attained in the individual oil droplets. In a good mayonnaise emulsion, the largest droplets will not be more than 6 to 8 microns in diameter and many will be in the range of 2 to 4 microns. In poor emulsions, most of the droplets may be 10 microns in diameter, or larger. Usually about 10% to 12% of air, by volume, is incorporated into the emulsion during the mixing operation.

All mayonnaise gradually becomes thinner with age, due to gradual coalescence of oil particles, and if kept for a sufficient length of time, will eventually separate more or less completely into two separate phases.

[3] J. W. Corran has shown that the powdered mustard in mayonnaise also acts as an emulsifying agent, and that its effect is antagonistic to the tendency of calcium soaps to reverse the emulsion type. See International Soc. Leather Trades' Chemists, *Emulsion Technology*, Chem. Pub. Co., New York. 1943, pp. 176–192.

The thinning and separation of mayonnaise is greatly accelerated by mechanical shock or vibration, such as occurs in shipment of the product. As stated previously, the emulsion will also be broken if it is subjected to temperatures low enough to cause extensive crystallization of the oil. However, mayonnaise with the emulsion broken is now seldom seen on the market.

Mayonnaise may be classed as a semiperishable product. It is sufficiently stable to keep for reasonable lengths of time without refrigeration, but it will not stand indefinite storage. Mayonnaise chiefly becomes unmerchantable, however, from breakdown of the emulsion or from oxidation, rather than from the action of microorganisms, whose growth is effectively inhibited by the acidity of the product.

(b) Manufacture

The initial mixing of mayonnaise is often carried out in relatively small batches, in bowls equipped with high-speed beaters. The usual procedure in mixing is as follows: (1) First, place in the bowl all the egg yolks, sugar, salt, and spices, and a portion of the vinegar and mix; (2) gradually beat in the oil; (3) thin out, by mixing in the remainder of the vinegar. This method of mixing is said to give a product of better consistency than is obtained by adding the entire amount of vinegar at the beginning of the operation. Gray, Maier, and Southwick[4] have made a study of the effect of the method of mixing on the consistency of the emulsion, and recommended that one-third of the vinegar be added initially in making mayonnaise containing 78% of oil. On the other hand, Brown[5] recommends that the mixture of eggs and dry ingredients be as stiff as possible when the oil is beaten in.

The temperature of the oil and other materials during the mixing also influences the body of the mayonnaise. A thin product results if the operation is carried out with materials that are too warm. Gray and Maier[6] who have investigated this phase of mayonnaise manufacture, suggest a temperature of 60° to 70°F. as most suitable. They found that the emulsion was increasingly thick with decreased temperatures down to 40°F. The lower temperature products lost much of their initial superiority over 60–70° products with slight aging, however, and the inconvenience of attempting to operate at temperatures below 60°F. was not judged to be worth while. However, Brown[5] recommends a 40°F. temperature.

Commercial products made in large establishments are often coarsely emulsified and then given a further homogenizing treatment in machines

[4] D. M. Gray, C. E. Maier, and C. A. Southwick, *Glass Packer*, *2*, 397–400 (1929).
[5] L. C. Brown, *J. Am. Oil Chem. Soc.*, *26*, 632–636 (1949).
[6] D. M. Gray and C. E. Maier, *Glass Packer*, *4*, 23–25, 40 (1931).

of the colloid mill type before they are packaged. The usual packages are glass jars, ranging in capacity from one-half pint to one gallon.

Various instruments have been devised for testing the important property of consistency in the mayonnaise emulsion. One device in common use is a modified form of the Gardner mobilometer[7] which was originally designed for testing paints, varnishes, and enamels. The mobilometer is in reality a special form of viscometer in which a weighted plunger equipped with orifices is pressed through the sample. Another suitable device is a special orifice type viscometer which utilizes air pressure rather than gravity to discharge the sample through a standard orifice. Kilgore[8] has devised a simple method which is particularly suitable for control work, since it involves nothing more than dropping a pointed rod or "Plumit" into a sample from a definite height, and noting the depth of its penetration.

The ability of a mayonnaise emulsion to resist mechanical shock is commonly evaluated by testing samples for a prolonged period in a laboratory shaking machine.

The suitability of different varieties of oil for mayonnaise manufacture has been discussed in a previous paragraph (Sect. D). The best mayonnaise oils are corn oil, sunflower oil, sesame oil, and well winterized cottonseed oil. Only the best grades of the different oils should be used. Mayonnaise manufacturers usually specify that oils should be low in free fatty acid content (*e.g.*, not over 0.03%), completely neutral in flavor and odor, and free from any trace of reaction in the Kreis test. The vinegar and spices used in mayonnaise do not serve, as one might suppose, to suppress or disguise the flavors of poorly deodorized or partially oxidized oils. They have the effect, rather, of accentuating any natural flavor that the oil may possess. For this reason, more strict neutrality is required in a mayonnaise oil than in almost any other oil or fat product.

2. Other Salad Dressings

In the grocery trade in the United States, the term "salad dressing," without qualification as to variety, refers to a product which consists essentially of mayonnaise mixed with a cooked starch paste. It is similar in appearance to mayonnaise, and somewhat similar in taste, and, although a cheaper product, is often confused with the latter.

The essential ingredients of salad dressing are eggs, vinegar, oil, spices, and starch and water. In general, the quality is determined by the oil content, which is quite variable. The better brands usually contain

[7] H. A. Gardner and A. W. Van Heuckeroth, *Ind. Eng. Chem., 19*, 724–726 (1927). D. M. Gray and C. A. Southwick, *Glass Packer, 2*, 17–19, 42, 77–81 (1929).
[8] L. B. Kilgore, *Glass Packer, 4*, 65–67, 90 (1930).

40–50% oil, although products as low as 20% in oil, or even lower, are not uncommon. A formula which is perhaps more or less representative of dressings of reasonably high oil content is given by Campbell[9] as follows (in oz.): corn starch, 5.25; water, 80.0; salt, 2.125; vinegar, 10.0; mustard, 0.75; cayenne pepper or paprika, dash; egg yolk, 13.33; and oil, 80.0. A cooked paste is prepared from the starch, water, and salt. The remaining ingredients are mixed as in the manufacture of mayonnaise, and then blended with the cooled paste. Finally, as in the manufacture of mayonnaise, the blend is put through a colloid mill or other homogenizing device before it is packaged. A number of plants are in operation in the United States in which the entire manufacturing operation is continuous, with the starch being cooked in closed steam-heated machines of the "Votator" type.[10]

There are a number of other prepared salad dressings on the market in the United States, but the volume of sales of these is unimportant in comparison with that of mayonnaise and salad dressing. A number of these dressings, and also certain "sandwich spreads," etc., utilize a mayonnaise or salad dressing base.

An interesting new patent covers a dry preparation of powdered egg yolks, citric or other organic acid, fat, spices, sugar, and gelatin or gelatinized flour, which may be reconstituted to form a salad dressing simply by the addition of water.[11]

[9] C. H. Campbell, *Canning Age, 14*, 316 (1933).
[10] J. V. Ziemba, *Food Inds., 21*, No. 3, 124–127. 200–201 (1949).
[11] M. H. Kimball, C. G. Harrel, and R. O. Brown (to Pillsbury Mills, Inc.), U. S. Pat. 2,471,435 (1949).

PLASTIC SHORTENING AGENTS

A. Introduction

The designation of plastic shortening agents is applied here to pure fats which are of such consistency that they may be readily spread, mixed, or worked. This class of fat products consists largely of lard or hog fat, and the vegetable or animal and vegetable products of lard-like consistency which have come to be known as shortenings. Excluded from the classification are leaf fat, suet, salt pork, or other fatty animal tissues, the so-called hard butters used in confectionery, and also butter and margarine, which are not pure fats, but mixtures or emulsions of a fat and an aqueous liquid.

1. Historical

Some knowledge of the history of the lard and shortening industries is essential to a full understanding of the problems involved in the technology of their products. Therefore, before proceeding to a description of the individual products a brief review will be presented of the development of these industries. For additional details regarding the history of the shortening industry the reader is referred to the monograph on this subject by Weber and Alsberg.[1]

The first oil or fat products used by man undoubtedly were rendered from the carcasses of wild animals. As animal husbandry became generally practiced, in a more advanced state of civilization, the body fat of domestic animals came to be an important article of commerce. In addition to their use as edible materials, animal fats found a wide variety of other applications, for example, as illuminants, lubricants, and materials for making soaps. Wild animals ceased to be an important source of fats at an early date. However, with the development of the whaling and sealing industries, the supply of domestic animal fats was supplemented by large quantities of marine oils of analogous origin.

As the various uses of fats became more highly specialized and standardized, the body fat of hogs, or lard, came to be the preferred fat for

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[1] G. M. Weber and C. L. Alsberg, *The American Vegetable Shortening Industry.* Food Research Institute, Stanford University, 1934.

edible purposes, whereas the other animal fats were utilized principally in nonedible products. This particular trend of specialization may have been in part due to the distinctive flavor of lard, which possibly is inherently more pleasing than that of beef or mutton tallow or marine oils. The chief reason, however, for the favor enjoyed by lard as an edible fat is undoubtedly the particular consistency of this fat. At ordinary temperatures, lard has very nearly the optimum consistency for the readiest incorporation into breads, cakes, pastries, and other leavened baked products. Tallow is too firm for this purpose, except at quite elevated temperatures, and marine oils are too fluid.

For many years, lard and other animal fats have not been primary products of animal husbandry, but by-products of the meat-packing industry. The extent to which lard is produced now depends purely upon the demand for pork. Consequently, the supply of lard is not directly related to the demand for this commodity.

For some time the production of lard has been far short of the demand for plastic shortening agents in the lard-consuming countries. This has stimulated the production and use of both vegetable and marine oils, which are now consumed in large quantities in the American and European countries which formerly depended almost entirely upon animal sources for their edible fats.

Since the people of these countries were accustomed to the use of fats rather than liquid oils, it was natural for the manufacturers of food products to seek means of converting the vegetable and marine oils to plastic products. Originally this was accomplished by blending a relatively large proportion of vegetable oil with a relatively small proportion of oleostearine or other very hard animal fat. Later the method of hardening oils by catalytic hydrogenation was developed. This process enabled the manufacturer to produce a plastic product entirely from a liquid vegetable oil, and also made it possible to produce shortenings and margarine from marine oils.

In Europe, the vegetable and marine oils are principally made into margarine, which is designed to have as nearly as possible the characteristics of butter. In the American countries, however, and particularly in the United States, the tendency has been rather to utilize these oils in the form of shortenings which more or less simulate lard.

Shortening is an American invention, growing out of the cotton-raising industry. The rapid expansion in the acreage of cotton grown in the United States, between the end of the Civil War and the close of the 19th century, resulted in large quantities of cottonseed oil being produced, as a by-product of the growing of cotton for lint. Shortenings were developed to provide an outlet for this oil.

The first shortenings, prepared by the blending of hard and soft fats,

were termed "lard compounds" or simply "compounds," and were frankly conceived and marketed as substitutes for lard. In the development of the shortening industry, the large American meat packers played a prominent role because of their control of the supply of hard animal fat which was an essential ingredient of the product. All the larger packers entered the field in order to market their tallow and oleostearine to the best advantage. A large proportion of the shortening manufactured continues to be made by meat-packing companies, in spite of the fact that much of their product is now of purely vegetable origin.

The introduction of the catalytic hydrogenation process into the United States, in about 1910, made the shortening manufacturer independent of the meat-packing industry, and initiated a new era in the manufacture of shortening. Thenceforth, the development of vegetable shortenings followed two divergent courses. The meat packers continued to manufacture shortenings of the compound or blended type, employing the hydrogenation process only for the manufacture of highly hardened oil or vegetable stearine, to serve as an occasional substitute for oleostearine. Since the packers were engaged in the shortening business purely as a sideline, and since the new shortenings were to some extent competitive with lard, it was natural that they were inclined to offer shortenings only as lard substitutes.

Other manufacturers of shortening, however, were prepared to exploit the possibilities of the product to the fullest possible extent, and, in consequence, to offer lard producers the most aggressive kind of competition. The early manufacturers of purely vegetable shortening were sufficiently far sighted to abandon the concept of shortening as a mere lard substitute and immediately to offer their product as a new food material, with properties admittedly different from the traditional properties of lard. The terms "lard compound" and "compound" were dropped and replaced by proprietary names which were not suggestive of any animal product.

In addition to advertising extensively, the vegetable-shortening manufacturers were also active in devising methods for improvement of the product. The crude cottonseed oil was more carefully refined and bleached than had been the general custom in the manufacture of compounds. New methods of deodorization involving the use of high temperatures and high vacua resulted in the removal of every trace of odor or flavor from the fat. Improved methods of solidifying, filling, and packaging the product were devised, to enhance its appearance and keeping quality.

One of the largest manufacturers of shortening adopted the practice of hydrogenating the entire mass of oil to the desired consistency, rather than stiffening the liquid oil by the addition of a small proportion of

highly hydrogenated material. This method of manufacture resulted in a product of considerably lower iodine value than ordinary blended shortening, and one of consequently improved stability. Subsequent improvements in the technique of hydrogenation enabled manufacturers steadily to reduce the iodine value of their shortening and increase its resistance

TABLE 59

PRODUCTION, EXPORTS, AND PRICES OF LARD, COTTONSEED OIL, AND SHORTENING IN THE U. S. (1920–1941)[a]

	Production, million pounds				Average prices during January of the year indicated, cents/lb.		
Year	Crude cottonseed oil	Short- enings, all types	Lard	Lard exports, million pounds	Crude cottonseed oil (tanks)	Compound- type shortening (tierces)	Lard (loose)
1920	1309	747	1943	635	19.7	25.2	22.6
1921	930	811	2092	893	6.1	12.4	11.8
1922	1003	784	2283	787	7.2	11.0	9.4
1923	980	751	2692	1060	9.8	13.4	10.8
1924	1404	830	2635	971	9.5	14.2	11.6
1925	1617	1153	2133	708	9.5	14.7	15.2
1926	1888	1141	2185	717	9.8	13.8	14.2
1927	1477	1179	2240	702	6.9	10.7	11.5
1928	1604	1143	2432	783	8.5	12.9	11.0
1929	1572	1220	2435	848	8.6	12.4	10.9
1930	1442	1211	2201	656	7.2	10.8	9.5
1931	1694	1171	2280	578	6.2	9.4	7.9
1932	1446	945	2353	552	3.2	6.3	4.6
1933	1303	953	2448	584	2.9	5.3	3.6
1934	1109	1204	2068	435	3.6	7.0	4.6
1935	1164	1547	1270	97	9.6	13.1	12.5
1936	1364	1587	1676	112	8.9	12.4	10.6
1937	1961	1595	1417	137	10.4	13.7	12.8
1938	1409	1514	1713	205	6.2	10.2	8.2
1939	1325	1404	1998	277	6.0	9.2	6.3
1940	1356	1190	2297	201	5.9	9.5	5.3
1941	1391	1418	2250	393	5.4	10.3	5.6

[a] Data compiled from U. S. Bur. Census, *Animal and Vegetable Fats and Oils*, 1938 to 1942, Washington, 1943, from U. S. Dept. Agr., *Agricultural Statistics*, 1942, and from publications of the Bureau of Agricultural Economics of the U. S. Department of Agriculture.

to oxidation. The superior neutrality, stability, and uniformity of the all-hydrogenated type of shortening found particular favor with commercial bakers. Eventually all of the shortening manufacturers, including the meat-packing companies, took up the manufacture of shortening of this variety for their baking trade, even though many continued to make only shortenings of the compound type for household consumption.

In the long-standing competition between lard and vegetable shortening, lard appears at present to be at a rather decided disadvantage.

Certain statistical data relative to the production and consumption of lard, cottonseed oil, and compound-type shortenings in the United States in the period 1920–1941 are recorded in Table 59. The prices listed in this table for the three fats are not strictly comparable. The cost of solidifying the fat and placing it in containers (tierces) is included in the price of compound shortening, whereas crude cottonseed oil and lard are quoted on a loose basis. The tiercing cost amounts to approximately one cent per pound. However, it will be seen that by 1920, compound shortening had attained a virtual parity in price with lard. Shortenings of the all-hydrogenated variety have at all times commanded a price substantially above that of compounds. The approximate parity in price between lard and compound shortening persisted for a number of years, during which the total production of lard amounted to between 2 and 2.5 billion pounds, of which about one-third was regularly exported.

Following the business recession beginning in 1929, exports of lard decreased, with the result that the price of lard dropped somewhat more drastically than that of compounds or cottonseed oil. By 1935, governmental control had restricted the production of both lard and cottonseed oil, and almost eliminated the former from export trade. The restriction of lard production was more severe than that of cottonseed oil, and was less quickly recovered after the relaxation of control measures. Consequently, until lard production again became normal, in about 1939, the price of lard again followed closely the price of compound shortenings.

In 1939, the production of lard again approached 2 billion pounds but exports lagged at less than 300 million pounds. The price of lard then fell far below that of compounds and closely approached that of the crude cottonseed oil from which these shortenings are principally manufactured. By late 1941, when prices of fats and oils were stabilized by governmental action, the price of prime steam lard in tierces at Chicago was 1.4 cents per pound under that of crude cottonseed oil in tank cars at the mills. Subsequent shipment of government purchased lard to Europe in large quantities increased the demand for this product, and resulted in the ceiling price of lard being raised to approximately that of crude cottonseed oil. In the period 1942–1946, exports were at the rate of 500–900 million pounds yearly. Since the removal of price controls in 1946, the price of lard has again been generally under that of crude cottonseed or soybean oil. During 1949, a period of relatively high lard prices, the average price of loose lard at Chicago was 11.3 cents per pound, as compared with 11.6 cents per pound for crude cottonseed oil at the mills.[1a] In August, 1949, average retail prices of butter, lard in 1-pound cartons, vegetable margarine in 1-pound prints, and all-hydrogenated

[1a] Bureau of Agricultural Economics, U. S. Dept. Agri., *The Fats and Oils Situation*, October, 1949, January, 1950.

vegetable oil shortening in containers other than cartons were 72 cents, 19 cents, 30 cents, and 33 cents per pound, respectively.[1a]

The high degree of favor enjoyed at present by the vegetable shortenings is doubtless due in part to their superior physical properties, as compared with lard. Much American lard is not only rather softer in consistency than is desirable, but is also nonuniform in consistency, due to variations in composition according to the feed of the hogs, and other factors. Also, lard does not cream well in the manufacture of cakes and sweet goods, and is much less resistant to deterioration through oxidation than good vegetable shortening. Good creaming and mixing properties, high stability, and uniformity are properties which are particularly desired by commercial bakers. The increased use of shortening agents in baked goods in recent years has caused a relative increase in the demand for shortenings.

TABLE 60

PRODUCTION AND CONSUMPTION (MILLIONS OF POUNDS) OF LARD (INCLUDING RENDERED PORK FAT) AND SHORTENINGS IN THE PERIOD 1942–1948[a]

	Lard						Shortenings	
	Produced				Used in	Civilian		Civilian
Year	By meat packers[b]	On farms[c]	Total	Exports[d]	manuf. products[e]	consumption[f]	Produced	consumption
1942	1724	676	2401	685	71	1689	1300	1237
1943	2080	785	2865	796	141	1678	1438	1234
1944	2367	687	3054	938	241	1583	1364	1147
1945	1311	755	2066	671	112	1510	1441	1175
1946	1344	794	2138	490	24	1645	1451	1409
1947	1722	704	2426	417	111	1816	1374	1338
1948	1680	676	2356	327	122	1885	1441	1411
1949	1923	629	2552	696	154	1754	1483	1431

[a] Bureau of Agricultural Economics, U. S. Dept. Agr., *The Fats and Oils Situation,* July, 1949, July–Aug., 1950
[b] Federally inspected establishments.
[c] Estimate.
[d] Including shipments to U. S. territories.
[e] Largely shortening, but including also margarine, soap, etc.
[f] Exclusive of consumption in manufactured products.

Another property of lard which now appears to be rather more of a liability than an asset is its distinctive flavor. Through the prolonged use of odorless and tasteless shortenings and cooking oils, a large and apparently growing segment of the American people has developed a distaste for all natural fat flavors save that of butter. If there is a continuation of the present trend toward the consumption of neutral fat products, it appears not unlikely that, in the United States, lard like the crude vegetable oils, may eventually constitute merely a raw material for the manufacture of edible products, rather than a primary edible material.

This possibility has been recently given color by the increased use of lard in shortenings and by the appearance of a considerable production of shortening products consisting of lard or lard and beef fat blends, which have been refined, stiffened by hydrogenation of the incorporation of hydrogenated fat, fortified with antioxidants, deodorized, and in some cases, superglycerinated, to make them comparable to all-hydrogenated vegetable shortenings.

2. Production and Consumption

Data on the production and consumption of lard and shortenings during a later period than covered in Table 59 are given in Table 60.

B. Plasticity in Fats

1. Physical Structure of Fats

A fat such as lard or shortening is to casual appearance a soft, but more or less homogeneous solid. Under the microscope, however, it can be seen to consist of a mass of very small crystals (Fig. 15), in which is enmeshed a considerable proportion of liquid oil. If the fat is more

Fig. 14. Photomicrograph (×80) showing typical crystal habit of a fatty compound. Tallow fatty acids slowly crystallized from a solvent. (Courtesy V. C. Mehlenbacher.)

carefully examined, with the assistance of an apparatus designed for micromanipulation, it will be seen that the crystals are not joined together to form a continuous structure, but that each is a separate and discrete particle, capable under the proper shearing stresses of moving independently of the other crystals. Thus the fat has the characteristic structure of a plastic solid.
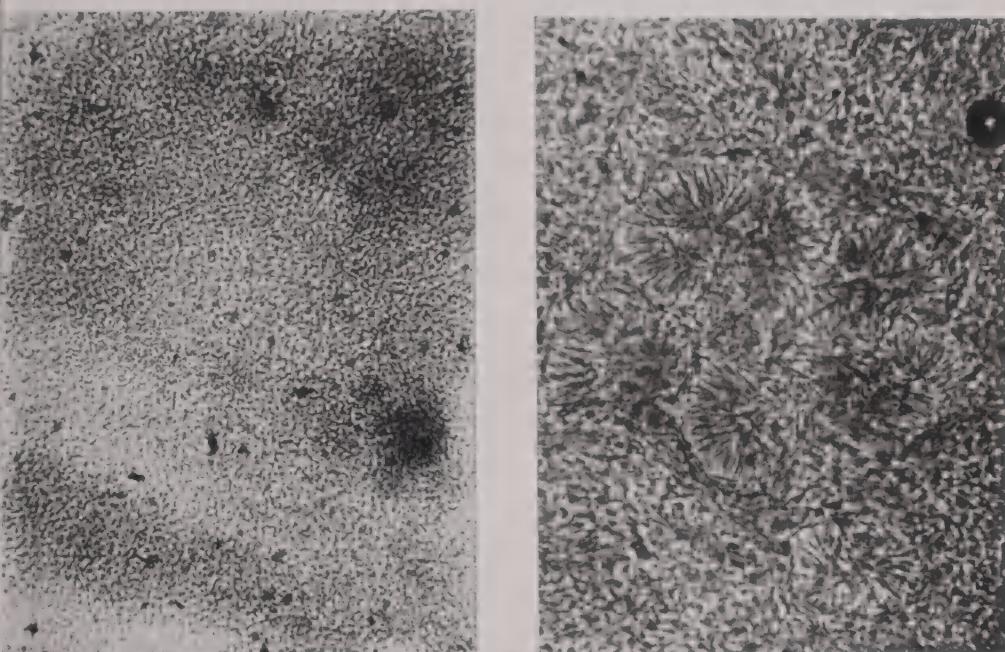
Fig. 15. Photomicrographs (×300) of: (left) hydrogenated cottonseed oil shortening, and (right) hydrogenated lard shortening; both solidified in commercial chilling equipment, but without the incorporation of air.

2. Theory of Plasticity[2]

The distinguishing feature of plastic substances is their property of behaving as solids and completely resisting small stresses, but yielding at once, and flowing like a liquid when subjected to deforming stresses above a certain minimum value. Thus a fat or other firm plastic material will not flow, collapse, or otherwise deform of its own weight, although it may be easily molded or dispersed into any desired form.

There are three conditions which are essential for plasticity in a material. First of all, it must consist of two phases. One of the phases must be solid and the other must be liquid, or else the two must be

[2] For a more complete treatment of this subject, see A. E. Bailey, *Melting and Solidification of Fats*, Interscience, New York, 1950.

capable of acting as solid and liquid. In the case of plastic emulsions, the disperse phase may actually be either an immiscible liquid or a gas. However, in their state of extreme subdivision the globules of liquid or gas are so powerfully restricted by the forces of surface tension as to behave as solid particles.

A second condition for plasticity is that the solid phase must be in a state of sufficiently fine dispersion for the entire mass to be effectively held together by internal cohesive forces. The solid particles must be small enough for the force of gravity on each to be negligible in relation to the adhesion of the particle to the mass, and the pores or openings
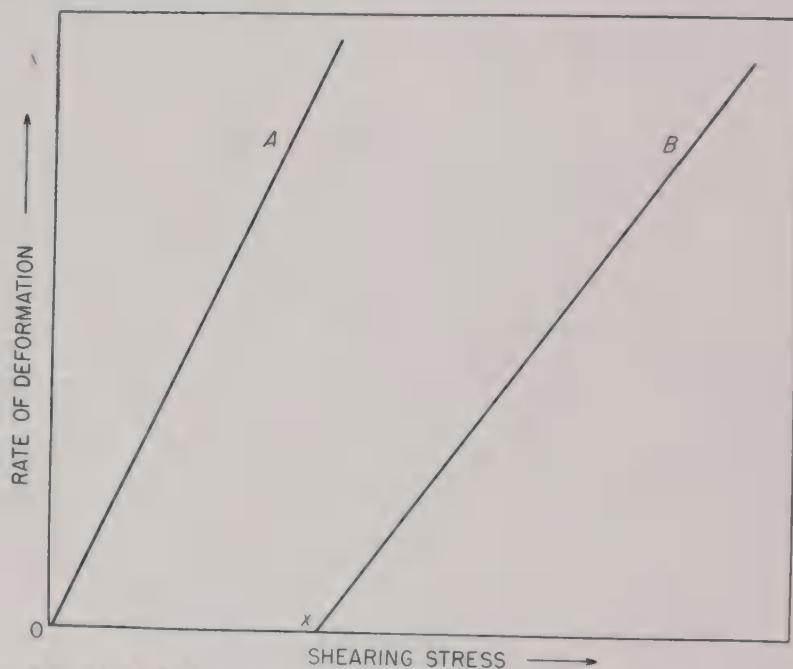
Fig. 16.   Ideal deformation curves of: (A) a viscous material, and (B) a plastic material; x denotes the yield point of the latter.

between the particles must be so small that there is a negligible tendency for the liquid phase to flow or seep from the material.

The third condition for plasticity is a proper proportion between the two phases. The solid particles must not be so few that the mass can flow without these particles forming interfering clots and jams. On the other hand, the solid particles must not be so preponderant as to form a rigidly interlocked structure.

According to the concept of plasticity developed by Bingham[3] and others, a plastic solid owes its peculiar properties to the tendency of its solid particles to form jams or arches which support the material against

[3] E. C. Bingham, *Fluidity and Plasticity*. McGraw-Hill. New York. 1922.

shearing stresses. Thus the application of small stresses (such as the force of gravity) results in no flow or movement. When sufficient force is applied to break these jams, however, the material abruptly yields and plastic flow occurs.

The fundamental difference between plastic and a merely viscous material is shown graphically in Figure 16, where the rate of deformation of each is plotted against the magnitude of the deforming stress. It will be seen that even a very slight stress causes some degree of deformation in a viscous substance; hence the consistency of such a substance is expressed simply by the *viscosity*, or the slope of the curve rising in a straight line from the origin. On the other hand, limited stresses are absorbed elastically in a plastic material, without permanent deformation occurring. Consequently, the consistency of the material is in effect made up of two components: (*1*) the yield value, represented in the graph by the horizontal distance from the origin to the lower end of the linear curve, and (*2*) the viscosity, represented as before by the slope of this curve. In fats, as in other plastics, high viscosities and high yield values go, in general, hand in hand. Careful independent evaluation of the two factors reveals that in different fats there is some variation in viscosity at a given yield value, and *vice versa*, according to the constitution of the fat.[4] However, such variation is not marked, and for practical purposes reference is generally made simply to the *consistency* of a fat, which may be considered more or less a composite of the two factors enumerated above.

The limits within which a material will be plastic depend somewhat upon the shape, average size, and size distribution of the particles. According to Bingham,[3] in the case of a material whose solid particles approximate the form of uniform spheres, the upper limit of the solid phase is close to that obtaining in cubical close packing, namely about 52.36% by volume. The lower limit varies considerably with the size of the particles and the character of the material, but is generally within the range of about 5 to 25%.

As the percentage of solids in a fat varies continuously with variation in the temperature, a large part of the effect of temperature on fat consistency can be ascribed to changes in the relative proportions of solids and liquid. However, it appears that another major factor is the effect of temperature upon the viscosity of the liquid phase, which may account for as much as 30–50% of the total consistency variation.[4]

Another factor which influences the firmness of a plastic material is the size of the solid particles. With other factors constant, the material will become progressively firmer as their size decreases, due to increasing

[4] P. Søltoft, *On the Consistency of Mixtures of Hardened Fats*, English translation by E. Christensen, Bjarne Kristensen-Bogtrykkeri, Copenhagen, 1947.

opportunity for the particles to touch and increased friction to be overcome in causing it to flow.

Long needle-like crystals, which tend to interlace, have a more pronounced stiffening effect than crystals of comparable size of a more compact crystal habit.

Other factors which may affect both the firmness of the material and the solid–liquid ratio within which it is plastic are the degree of mutual attraction of solid particles, and their consequent tendency to form aggregates, the extent to which the liquid phase lubricates the solid particles at their points of mutual contact, and the rigidity of the particles

In so-called thixotropic materials the consistency may decrease while the material is being stirred or otherwise worked, returning slowly to its original value when the material is allowed to rest. This effect is caused by the solid particles either becoming temporarily oriented while being worked or temporarily losing a portion of their mutually cohesive forces.

3. FACTORS INFLUENCING CONSISTENCY

(a) *Content of Solid Material*

The factor most directly and most obviously influencing the consistency of a fat is the proportion of the material in the solid phase; the fat, of course, becomes firmer as the solids content increases. Methods are not available for determining the percentage of solids in a fat with a high degree of accuracy.[5]   However, from the best available evidence is appears that lard, shortenings, etc., begin to have sufficient body to hold their shape well with a solids content (by weight) in the neighborhood of 5%, and become inclined to crack rather than flow under stress when the solids content rises to something like 40–50%. This range is, of course, somewhat greater than the range within which such fats are easily spread or worked in mixing operations. The large effect upon the consistency of a comparatively slight variation in solids content is somewhat remarkable. A typical shortening, for example, will have the best consistency for easy mixing or working only within a solids content of about 15–25%, and an increment of as little as 1% in the percentage of solids will have a noticeable effect upon the consistency.

Tabulations of consistency (as measured by micropenetrations) *vs.* estimated solids content (dilatometric) are given in Table 61 for typical samples of lard and a shortening of the all-hydrogenated type, consisting

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[5] Estimates of percentages of solids may be made from either calorimetric or dilatometric data; uncertainties result from the variable heats of fusion and melting dilations of different triglycerides.

of partially hydrogenated vegetable oils blended with a minor proportion of a highly hydrogenated oil.

TABLE 61

MICROPENETRATIONS AND ESTIMATED SOLIDS CONTENTS AT DIFFERENT TEMPERATURES OF TYPICAL SAMPLES OF LARD AND SHORTENING

Temp., °C.	American lard		European lard		Shortening[a]	
	Micropen., mm./10[b]	Solids, %	Micropen., mm./10[b]	Solids, %	Micropen., mm./10[b]	Solids, %
50	—	0	—	0	—	0
45	—	0.5	—	2.5	—	2.9
40	—	2.0	—	5.5	—	5.7
35	—	4.5	—	7.5	336	9.4
30	378	10.5	—	14.5	212	12.9
25	137	21.0	—	26.5	101	14.0
20	105	26.0	—	32.5	45	16.7
15	73	29.0	—	37.5	24	21.7
10	41	32.0	—	—	16	27.8
5	—	—	—	—	—	31.4

[a] Shortening (Crisco) of the all-hydrogenated type, consisting of partially hydrogenated vegetable oil stocks blended with a small proportion of highly hydrogenated oil.
[b] By the method of R. O. Feuge and A. E. Bailey, *Oil & Soap*, 21, 78–84 (1944).

An important part of the technology of edible fats is concerned with the blending of glycerides in such a manner that the fat product will soften and melt or remain plastic and workable within suitable ranges of temperature. For the plastic shortening agents to be treated here, a maximum plastic range is usually desired. In general, long plastic ranges are obtained in mixtures of glycerides of widely different melting points, with the higher melting constituents being present in minor amounts. A short plastic range, with sharp softening and melting, results when the higher melting glycerides consist of a single class melting within a close range, and when these glycerides predominate over those of low melting point.

In common with other organic compounds of high molecular weight and considerable viscosity, triglycerides are given to supercooling markedly, and sometimes very persistently. A supercooled fat, in which the liquid and solid phases have not come to equilibrium, will, of course, contain less solids and be softer than normal fat at the same temperature.

(b) Size of Crystals

As indicated previously, the consistency of a plastic material is influenced by the size of the solid particles as well as their total volume; the material becomes progressively firmer as the average size of the particles decreases, and softer as their size increases.

It is for this reason that "grainy" lard is softer than "smooth" lard,

and shortening melted and slowly resolidified is softer than the same product after it is initially solidified on a chill roll or in the Votator chilling machine. In the commercial preparation of both lard and shortening, the fat is ordinarily chilled very rapidly, so that the crystals will be as small as possible. The production of fine crystals extends the plastic range of the product, and gives it a smooth appearance. Thus commercial methods of manufacture result in shortening products of the maximum degree of firmness.
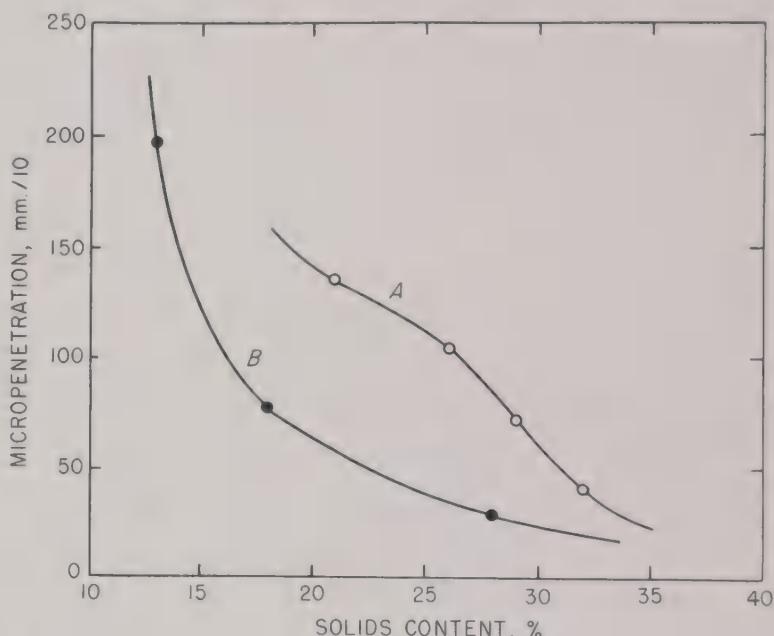
Fig. 17. Relationship between solids content and consistency in: (A) lard, and (B) oleo oil (beef fat).

The various hydrogenated vegetable oils, and also tallows and tallow derivatives, all form crystals of about an equal size when chilled rapidly. Their crystals are so small that it is difficult to form any accurate estimate of their size, but they appear to be of the order of perhaps 2 or 3 microns in length. Lard, however, has the peculiar property of solidifying under the same conditions in quite large crystals. The characteristically coarse crystal structure of lard is particularly well observed after slight hydrogenation of this fat (Fig. 15). Many crystals of hydrogenated lard are certainly in excess of 20 microns in length. If it is assumed that the crystals of lard and hydrogenated lard are 5 times as large in each dimension as those of vegetable shortenings, it follows that the shortening will contain 125 times as many crystals as lard of an equivalent solid glyceride content.

The low "stiffening power" of lard crystals, in comparison with the

rystals of other fats, is evident from the figures in Table 61, and more particularly from the comparative data on lard and beef fat (oleo oil)[5a] which are presented graphically in Figure 17.

(c) Persistence of Crystal Nuclei

In the handling and storage of plastic products subsequent to their solidification, considerable variations in temperature are inevitable. Each time that the temperature rises, a portion of the solidified fat becomes liquid, and, as the fat cools, a portion of it again becomes solid. If the variation in temperature is at all large, by the time the fat is ready for consumption the greater portion of its solid glycerides may well consist of resolidified crystals rather than the crystals originally occurring in the fat.

The cooling which takes place under such conditions is of course very much slower than the cooling applied to first solidify the fat. Since slow cooling normally results in the formation of coarse crystals, the consistency of a fat might be expected to be largely determined by the extent to which it had been previously heated and softened. The consistency of fats is in fact dependent to some extent upon their previous heat treatment, but not nearly to the extent which might be expected. If a sample of newly solidified shortening is immediately placed in a constant temperature bath at 70°F., it will become somewhat harder than a similar sample tempered at 85°F. for 24 hours and then brought to a temperature of 70°F. If the sample is once so tempered, however, it may subsequently fluctuate widely in temperature (e.g., between 40 and 90°F.) and yet always revert to substantially the same consistency at 70°F.

The ability of fats thus to retain their original crystal form through fluctuations in temperature apparently arises from the circumstance that the melting or dissolving fat crystals are capable of leaving behind invisible nuclei which serve as starting points for the development of new crystals when the fat is again cooled.

(d) Other Factors

In a blend of soft oils with very hard fats the crystals of trisaturated glycerides appear to have substantially greater stiffening power than the crystals of disaturated glycerides in a partially hydrogenated or other more homogeneous material. Presumably, they are more rigid and less easily deformed under the influence of shearing stresses. Søltoft[4] has noted that such blends also have a slightly higher viscosity for a given yield point.

It has been shown[5b] that trisaturated glycerides have a more pro-

[5a] W. S. Singleton and A. E. Bailey, Oil & Soap, 22, 295–299 (1945).
[5b] P. J. Mitchell, Jr. (to Procter and Gamble Co.), U. S. Pat. 2,521,242 (1950).

nounced stiffening effect in the β'-form than in the β-form, because of the more compact crystal habit of the latter. Mixed trisaturated glycerides have a greater stiffening effect than a fat composed substantially of a single fatty acid,[5c] presumably because they assume the β-form less readily.

Certain effects of the heat treatment of plastic fats seem to have no direct relation to the normal influence of temperature variations on the relative proportions of solids and liquid. "Tempering" of a shortening or other fat at a temperature somewhat short of the melting point has a permanent softening effect, and also appears to produce crystals of greater hardness or rigidity, inasmuch as it improves the "creaming" qualities of the fat (see page 301). Tempering may be interpreted as an "unmixing" process, wherein crystals made up of molecules of a number of different glycerides (differing considerably in melting point) are reformed to give a smaller proportion of crystals of greater homogeneity.

Mechanical working may affect the consistency of a plastic fat considerably. Commercially solidified shortening issuing from the chilling machines is always kept in a state of agitation until crystallization in the supercooled material is substantially complete; failure to maintain agitation produces an abnormally hard product, presumably from growing together of the crystals in a continuous lattice. Fats exhibit the phenomenon of thixotropy to a considerable degree, i.e., they become temporarily softer during mixing operations or other working. The precise cause of thixotropy in fats is not known; it may be the result of slight deformation of the crystal particles during working, of a slight tendency of the crystals to adhere or grow together when at rest, or orientation of the crystals under stearing stress may be an important factor.

4. Evaluation of Consistency or Plasticity

As has been mentioned previously, it is possible to evaluate separately the yield value of a fat and the viscosity of the fat after the yield value is exceeded. However, the techniques for such evaluation are somewhat involved, and in industrial laboratories the practice is to determine in arbitrary units a value for *consistency* which is dependent upon both yield value and viscosity.

There is no standardization whatsoever of the methods or devices used for measuring consistency, and there are virtually as many different systems of consistency evaluation as there are manufacturers of shorten-

[5c] N. W. Ziels and W. H. Schmidt (to Lever Bros. Co.), U. S. Pat. 2,530,596 (1950).

ing.[6] From the standpoint of simplicity of the instruments and the ease and rapidity of making the tests, the penetration technique of measuring consistency has much to recommend it. The measuring operation is particularly simple and easily carried out if a penetrometer is used with a needle or other penetrating device which is actuated simply by the force of gravity.

In the succeeding pages, consistency will principally be discussed in terms of macropenetrations by the Goddard-Hewes penetrometer[7] in the case of commercially solidified materials. Where other fats have been examined, or where it has been desirable to solidify that fat in a standard manner and thus make the examination independent of the manufacturer's method of solidification, the micropenetrometer first proposed by Freyer[8] and modified and standardized by Feuge and Bailey[9] has been used for most consistency measurements.

Ordinarily, samples of the fat to be examined are tempered in constant temperature air or water baths at several different temperatures covering the greater part of the plastic range. From measurements on these samples a penetration or consistency curve is constructed, which represents the over-all body characteristics of the product.

5. Importance of Plasticity in Edible Fats

There are a number of fat products in which the property of plasticity may be regarded as essential. One class of such products consists of butter, margarine and other so-called table spreads. The spreading of butter or margarine on bread is a perfect example of plastic flow. Other edible products in which plasticity is highly important are the fats which are used as shortening agents in baked products. When plastic fats are mixed into a batter or a dough, they are capable of being extended to form streaks and films, whereas under like conditions liquid oils can only be dispersed in the form of droplets or globules. Fat films naturally lubricate larger surfaces in the dough than do spherical droplets of oil, and thus have a more pronounced shortening effect.

In the process of mixing doughs, plastic fats, unlike liquid oils, are able to enclose and hold considerable quantities of air. In the manufacture of certain baked products, particularly cakes and other goods containing much sugar, the leavening action of this air is very important. The subject of plasticity, as related to the baking properties of shortening materials, is discussed at length in the chapter devoted to bakery products.

[6] See A. D. Rich, *Oil & Soap*, *19*, 54–57 (1942).
[7] W. R. Goddard and C. K. Hewes, U. S. Pat. 1,703,270 (1929).
[8] E. Freyer, *Ind. Eng. Chem.*, *Anal. Ed.*, *2*, 423–424 (1930).
[9] R. O. Feuge and A. E. Bailey, *Oil & Soap*, *21*, 78–84 (1944).

C. Lard and Other Animal Fats

1. Varieties of Lard

Most of the lard produced in the United States is wet-rendered in closed tanks under steam pressure. Lard of standard quality produced by this method of rendering is designated as *prime steam lard.*

The so-called refined lard of commerce, which is marketed in tierces, drums, cans, tubs, pails, and cartons, is not refined in the sense that vegetable oils are refined, since it receives no treatment with caustic soda or other alkali. This product consists simply of prime steam lard which has been dried, clarified (possibly with some degree of bleaching), and solidified. Unless cartons and other packages of lard are given some specific designation, such as "kettle-rendered lard," "leaf lard," etc., their contents may be considered to be ordinary prime steam lard. Such lard is very often stiffened, however, by the addition of hydrogenated lard stearine or "flakes."

TABLE 62

ANALYSES OF REPRESENTATIVE SAMPLES OF PRIME STEAM LARD, DRY-RENDERED LARD, AND LEAF LARD

Analysis	Prime steam lard	Dry-rendered lard	Leaf lard
Iodine value	68.2	68.5	58.5
Free fatty acids, % as oleic	0.30	0.25	0.15
Color, Lovibond scale	10Y–1.0R	15Y–1.8R	10Y–1.2R
Stability, hrs. by the Swift method	8.0	8.5	16.0
Titer, °C.	38.2	37.5	41.5
Micropenetration, mm./10, at:			
50°F.	52	55	28
70°F.	110	120	58
80°F.	155	180	75
90°F.	275	325	210
95°F.	a	a	360

a Too soft to determine.

In some plants ordinary lard is produced by a dry-rendering process, rather than steam rendering. Such lard cannot be labeled as prime steam lard, although it is sold and used for the same purposes. *Dry-rendered lard* often has a "cooked" flavor, somewhat different from that of prime steam lard, and is usually somewhat darker in color because it contains traces of colloidally dispersed protein materials. Otherwise it is identical with the more common prime steam lard. The flavor of dry-rendered lard is preferred by some users.

Leaf lard refers specifically to lard rendered from the internal "leaf fat" of the animal. Leaf lard is on the average perhaps 10 units lower in iodine

value than ordinary prime steam lard from the same animal, and correspondingly firmer. Leaf lard is almost always rendered by a dry process in an open kettle. The method of rendering gives the product a distinctive flavor. In addition to being firmer than ordinary lard, leaf lard also has somewhat better keeping qualities. It is in chief demand as a fat for household use, and it ordinarily sells at a slight premium over ordinary lard. A limited amount of kettle-rendered lard is produced from fatty tissues other than leaf fat.

Neutral lard is a special product made by wet rendering selected stock at a low temperature, with the object of producing a very mild flavored fat for margarine manufacture. Since the development of efficient processes for deodorizing vegetable oils, the production of this variety of lard has greatly declined.

2. Variations in Composition of Lard

The composition and resulting characteristics of lard are subject to very wide variation. They are affected by the feed of the hog, and are different in lard rendered from different parts of the carcass of the same animal.

The hog has, to a high degree, the ability to assimilate ingested fat with little change in its component fatty acids. Most of the vegetable oils which occur in the feed of the hog are more highly unsaturated than the fat synthesized by the animal from proteins or carbohydrates. Consequently, the degree of unsaturation of hog fat depends to a great extent upon the amount of oil in the feed of the animal and its fatty acid composition.

An extensive investigation of the factors influencing the composition of lard has been carried out by Ellis and co-workers. These investigators were chiefly concerned with the consistency of hog fat in its relation to the production of soft or "oily" bacon and other meat products.

It was found by Ellis and Hankins[10] that there was a progressive decrease in unsaturation in the fat of corn-fed hogs during the growth of the animal. Certain data of these workers relative to hogs of different ages fed on a diet of skim milk and corn are recapitulated in Table 63. The change in the fat of the hogs during the period of growth was ascribed to the observed fact that the rate of fat deposition steadily increased during this period. This would lead to a progressively larger proportion of the fat being synthesized from carbohydrates rather than being derived from ingested oil in the corn fed to the animals. In this and succeeding studies the actual consistency of the fat was observed to be closely related to its iodine value.

[10] N. R. Ellis and O. G. Hankins, *J. Biol. Chem.*, *66*, 101–122 (1925).

TABLE 63

VARIATIONS IN FAT OF HOGS DURING GROWTH OF ANIMALS. COMPOSITION AND CHARACTERISTICS OF COMPOSITE BODY FAT OF HOGS RAISED ON DIET OF SKIM MILK AND CORN[a]

Approximate age of animals	Approximate weight of animals, lbs.	Titer of fat, °C.	I.V. of fat	Composition of fatty acids, %		
				Satd.	Oleic	Linoleic
6 weeks	—	37.0	72.5	33.2	54.5	12.3
10–12 weeks	—	37.5	71.0	31.4	54.8	13.8
5 months	70	37.8	66.1	36.9	51.4	11.7
6 months	100	37.9	63.2	37.3	53.9	8.8
7 months	170	39.2	59.7	38.4	54.3	7.3
8 months	225	39.1	58.8	38.6	54.4	7.0

[a] From the data of N. R. Ellis and O. G. Hankins, *J. Biol. Chem.*, *66*, 101–122 (1925)

Ellis and Isbell[11] examined the fat of hogs fed on a wide variety of diets. Some of the results of their experiments are summarized in Table 64. It is noteworthy that the ingestion of different oils leads to distinctive arrangements in the proportions of the lard fatty acids. Thus, the difference between the lard derived from corn-fed hogs and hogs fed on brewer's rice and tankage is in the relative proportions of oleic and linoleic acids; the contents of saturated acids are substantially the same. The feeding of either peanuts or soybeans produces a very soft lard, but the proportions of the fatty acids are very different in the two cases. A trace of linolenic acid was detected in the fat of the soybean-fed hogs.

TABLE 64

EFFECT OF DIET ON FAT OF HOGS. COMPOSITION AND CHARACTERISTICS OF COMPOSITE BODY FAT OF HOGS RAISED ON DIFFERENT FEEDS[a]

Feed	Brewer's rice with tankage	Corn, with tankage	Peanuts (grazed)	Soybeans (grazed)
Oil content of feed, %........	0.8	4.3	33.1	17.5
Iodine value of oil...........	100	126	93	128
Analysis of fat:				
Iodine value..............	54.7	60.8	89.6	93.2
Refractive index at 40°C....	1.4585	1.4590	1.4625	1.4630
Melting point, °C..........	37.3	39.1	19.4	26.0
Titer, °C.................	40.0	40.3	28.1	33.9
Saturated acids, %........	39.3	39.3	20.6	27.2
Oleic acid, %.............	58.7	52.1	58.0	40.8
Linoleic acid, %...........	2.0	8.6	21.4	32.0

[a] From the data of N. R. Ellis and H. S. Isbell, *J. Biol. Chem.*, *69*, 219–248 (1926).

It was found by Ellis and Zeller[12] that hogs could be raised to a good weight and condition on a high protein diet almost completely devoid of fat. Lard derived from such hogs was extremely firm and contained but a

[11] N. R. Ellis and H. S. Isbell, *J. Biol. Chem.*, *69*, 219–248 (1926).
[12] N. R. Ellis and J. H. Zeller, *J. Biol. Chem.*, *89*, 185–197 (1930).

fraction of one per cent of linoleic acid. However, this lard, like that
examined in preceding studies, contained traces of arachidonic acid.

Inclusion of cottonseed oil in the diet of the hog has the peculiar effect
of increasing the iodine value of the lard and at the same time making
it firmer, through its marked tendency to raise the stearic acid content.[11a]

European lard is ordinarily somewhat lower in iodine value and firmer
than American prime steam lard, due to the widespread use in European
countries of skim milk and other feeds of low fat content. Much of the
lard produced in Europe has an iodine value below 60, whereas Ameri-
can prime steam lard from hogs fed on the usual diet of corn with a supple-
ment of tankage will have an iodine value which is seldom below 65 and
often above 70.
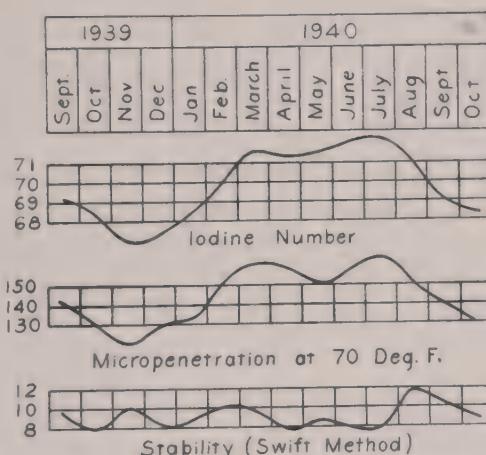
Fig. 18.   Seasonal variations in the characteristics of cutting lard.

Soybeans are seldom fed to hogs in any quantity, but it is common prac-
tice in certain sections of the southern United States to fatten hogs by
grazing them in fields of peanuts. The extremely soft fat from such ani-
mals must be stiffened by the addition of considerable percentages of lard
stearine before it can be packaged in cartons or used as a plastic fat. It
is not uncommon for prime steam lard from peanut-fed animals to have an
iodine value of 90 or higher.

A rather pronounced seasonal variation has been observed by the author
in the lard from hogs received at a middle-western packing house (see
Fig. 18). The iodine value is at a maximum in the summer and at a mini-
mum in the late fall, with a spread of approximately 5 units between the
average values for the high and low months. This variation in iodine
value is accompanied by a parallel variation in the consistency of the lard,
but there appears to be little or no correlation between iodine values and
the stability of the fat.

The iodine value of fat from a single animal is progressively higher from the internal organs outward toward the skin. Thus the leaf fat of a hog produces lard with the lowest iodine value, and the back fat produces lard with the highest iodine value. Since the same proportional amount of fat is usually taken from all parts of the carcass for the manufacture of prime steam lard, this circumstance does not result in any great degree of variation in the iodine value in ordinary packing house practice. However, changes from time to time in the methods of cutting the carcass and trimming the cuts may affect the characteristics of the lard to some degree. The weight and degree of fatness of the animal have something to do with the character of the lard. Heavy and fat hogs have a higher ratio of outer to internal fat than lighter and less fat animals.

In federally inspected establishments in the United States the total yield of lard and rendered pork fat per animal slaughtered is usually between 30 and 35 pounds, with cutting practices being such as to produce the heaviest yields when pork is relatively cheap and plentiful.

3. CONSISTENCY OF LARD

The factors influencing the iodine value of lard otherwise affect its consistency, as these two properties are related. Differences in the unsaturation of lard amounting to two or three iodine units are not always re-
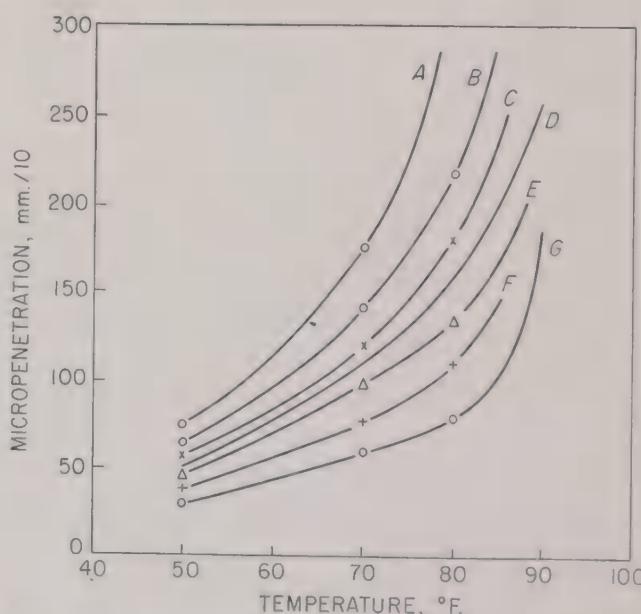
Fig. 19. Micropenetrations of typical samples of lard: (A), (B), and (C), cutting lard of different degrees of hardness; (D) mixture of cutting and killing lard; (E) killing lard; (F) mixture of killing and leaf lard; (G) leaf lard.

flected in the consistency of the product, but in general the firmness of lard is in inverse proportion to its iodine value.

In the large packing houses, it is common practice to produce two varieties of prime steam lard, namely "killing lard" and "cutting lard." The killing lard is obtained from fatty stock which is removed from the carcass at the time the animal is killed. Since a large portion of the killing fat is trimmed from the internal organs of the animal, the lard from this fat is relatively firm and low in iodine value. The cutting lard is rendered from stock obtained from the cutting floor, where the chilled carcass is divided into the various pork cuts. As this stock largely consists of fat trimmed from beneath the skin, cutting lard is softer and higher in iodine value than killing lard.

The usual ratio of killing to cutting lard produced is about 35 to 65. Prime steam lard usually consists of a mixture of these two varieties of lard in approximately these proportions.

Variations in the consistency of different samples of lard are illustrated by the micropenetration curves of Figure 19. These curves represent a variety of lards, ranging from a very soft cutting lard to a normal leaf lard. All of the lards of this series were rendered from corn-fed animals. Peanut-fed, or other "oily" hogs, produce lard considerably softer than the softest lard of the series. Most European lard would approach the consistency of the leaf lard. Leaf lard from corn-fed hogs is, incidentally, quite uniform in consistency and appears to be less subject to variation than the outer fat of the animals.

4. Adjustment of Consistency

Since the consistency of ordinary American prime steam lard is rather softer than is desirable, particularly when the product is destined for export to Europe, it has become common practice to stiffen prime steam lard by the addition of a small proportion of hydrogenated lard stearine. The stearine is prepared by deodorizing lard which has been refined and then hydrogenated to a low iodine value (usually 10 or below). It usually has a titer of 59–61 and is added in amounts ranging between about 4 and 8%.

For purposes of control it is convenient to combine the micropenetrations at 50°, 70°, and 80°F. into a single figure which gives approximately equal weight to the consistency at each temperature. Such a figure is the "consistency index," which is defined as follows:

where a, b, and c are the micropenetrations in tenths of millimeters at 50°, 70°, and 80°F., respectively:

$$\text{consistency index} = (7a + 3b + 2c)/10$$

Leaf lard usually has a consistency index quite close to 50. The index
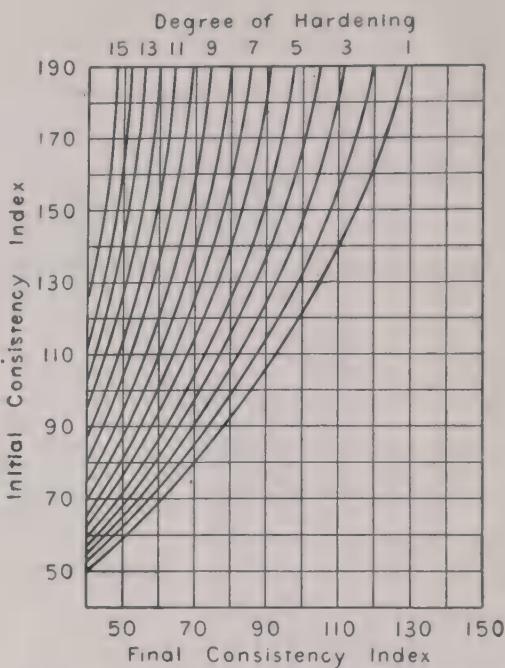
Fig. 20. Chart I for adjustment of the consistency
of lard: change in consistency index corresponding to
different degrees of hardening.
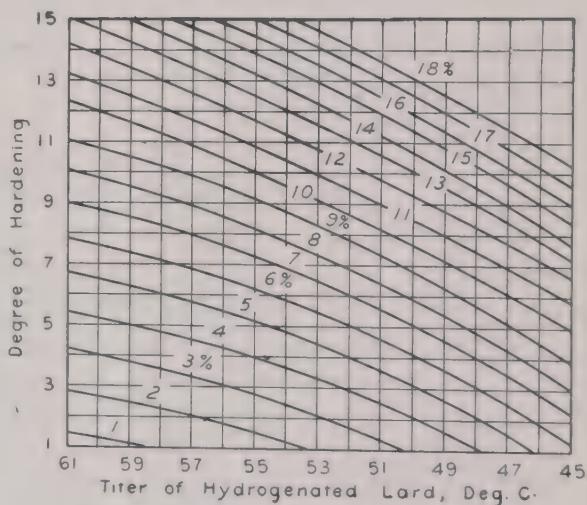
Fig. 21. Chart II for adjustment of the consistency of
lard: amount of hydrogenated lard stearine to be incorpo-
rated to attain different degrees of hardening.

of killing lard is usually between 75 and 100, whereas that of cutting lard
is usually between 110 and 150. However, it may be 160 or 170, or in ex-
ceptional cases even higher.

Since hydrogenated lard stearine may vary in its hardness and conse-
quent stiffening properties, and since lards of different consistencies re-

quire different degrees of stiffening, selection of the proper amount of stearine to be added is often a matter of some difficulty.
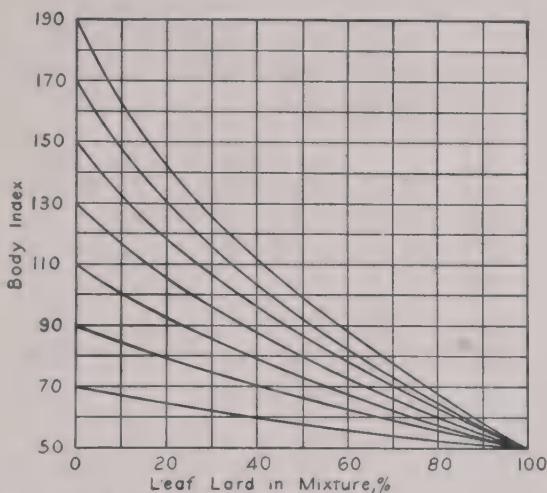
Fig. 22. Chart III for adjustment of the consistency of lard: amount of leaf lard to be incorporated to produce different changes in the consistency index.
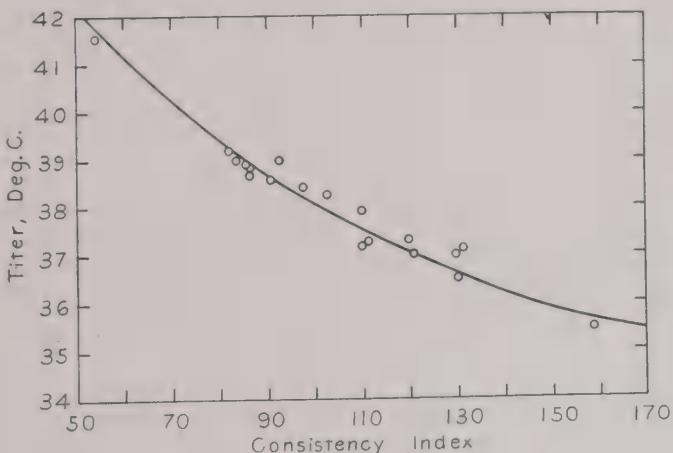
Fig. 23. Relationship between consistency index and titer of lard.

The charts of Figures 20 to 21 have been found useful as a guide to the amount of hydrogenated lard stearine to be added for converting lard from one consistency index to another. The curves of Figure 20 represent 15 arbitrarily selected "degrees of stiffening." The curves of Figure 21 represent the same 15 degrees of stiffening, in terms of percentages of lard stearine of various titers. A single example will suffice to show the manner in which the charts are used. Suppose, for example, that it is desired to stiffen lard with a consistency index of 140 to a consistency index of 70,

by the addition of 52° titer stearine. Reference to Figure 20 will reveal
that the desired change in consistency involves 8th degree stiffening. From
Figure 21 it may be seen that stiffening of the 8th degree will be obtained
by mixing approximately 9% of 52° titer stearine with 91% of the soft
lard.

If it is desired to effect a comparable stiffening by adding leaf lard rather
than lard stearine, Figure 22 may be similarly used as a guide.

The titer of a lard is a quite reliable indication of its consistency, pro-
vided that it contains no hydrogenated lard. Hydrogenation of lard, or the
addition of lard stearine to lard, stiffens the product to a greater degree
than is indicated by the change in the titer. The average relationship be-
tween the titer and the consistency of normal lards is shown graphically
in Figure 23.

5. STABILITY OF LARD

Lard is much less stable than equally unsaturated hydrogenated vege-
table oil shortenings. In accelerated oxidation tests by the Swift method,
even the more stable prime steam lards, with iodine values of 62 or 63, will
seldom keep longer than about 10 to 12 hours. Hydrogenated cottonseed,
soybean, or peanut oils of the same iodine value will keep 75 to 150 hours.

The limited resistance of lard to oxidation is caused by its lack of
natural antioxidants. Some progress has been made in recent years in im-
proving the stability of lard by more careful processing. However, a very
limited stability, in comparison with vegetable shortenings, is inherent
in the product in its pure state.

Various antioxidants from other edible plant and animal materials have
been proposed for addition to lard to improve its keeping qualities. These
include tocopherols and also phosphatides from peanut oil,[12a] corn oil,[13]
cottonseed oil,[13] soybean oil,[14] and the brain tissues and other tissues of
animals.[15]

Actually, phosphatides from any source are of little benefit in ordinary
lard. In the absence of tocopherols or other antioxidants of the phenolic
type, phosphatides improve the stability of lard but little. They tend to
cause the fat to foam, and also are inclined to produce a fishy odor in the
fat after the latter has become slightly oxidized. Due to their foam-
producing tendencies, phosphatides are not usually added to any fat in
greater amounts than a small fraction of one per cent.

[12a] C. L. Bibby, *Food manuf., 20*, 441–443, 448 (1945).
[13] B. H. Thurman (to Refining, Inc.), U. S. Pat. 2,201,063 (1940).
[14] H. Bollman, U. S. Pat. 1,464,557 (1923).
[15] W. F. Douglass (to Cudahy Packing Co.), U. S. Pat. 2,071,457 (1937).

Patents have been issued covering the addition of minor amounts of various vegetable oils to lard. These vegetable oils include palm oil,[16] hydrogenated sesame oil,[17] crude cottonseed oil,[18] crude soybean oil,[19] hydrogenated soybean oil,[20] and kapok oil.[21] The steam distillate resulting from the deodorization of sesame oil has also been patented,[22] as well as products from the deodorizer scums of other oils, with or without hydrogenation.[23]

In general, the vegetable oils may be said to be somewhat more effective in promoting the stability of lard than phosphatides.[24] From 5 to 10% of one of the above oils will usually more than double the accelerated keeping time of lard or hydrogenated lard. However, a fat containing this proportion of a vegetable oil is actually a compound, rather than a true lard, and cannot be labeled and sold as lard.

Patents[25] have been issued on oat flour and a great variety of other solid vegetable substances for incorporation into lard to improve its stability. However, there are obvious disadvantages in the use of any solid material for this purpose.

Additional natural antioxidants which have been recommended for lard and other edible fats include Southern sweet gum,[26] licorice resin,[27] tannins,[28] quercetin and other flavones,[29] "Kamala," a vegetable dye,[30] and norconidendrin, a wood pulp by-product.[31] Pure compounds which have antioxidant properties and apparently lack objectionable flavor or toxicity are hydroxychromans, hydroxycoumarans, and similar compounds related to the tocopherols,[32] caffeic acid[33] and hydrocaffeic acid

[16] R. C. Newton and W. D. Richardson (to Swift & Co.), U. S. Pat. 1,890,585 (1933).

[17] D. P. Grettie (to Swift and Co.), Brit. Pat. 395,971 (1933).

[18] D. P. Grettie and R. C. Newton (to Swift and Co.), Brit. Pat. 415,205 (1934).

[19] D. P. Grettie (to Industrial Patents Corp.), U. S. Pat. 2,052,289 (1936).

[20] D. P. Grettie (to Industrial Patents Corp.), U. S. Pat. 2,201,692 (1940).

[21] V. C. Mehlenbacher (to Industrial Patents Corp.), U. S. Pat. 2,108,922 (1938).

[22] D. P. Grettie (to Industrial Patents Corp.), U. S. Pat. 2,095,740 (1937).

[23] K. C. D. Hickman (to Distillation Products, Inc.), U. S. Pats. 2,349,269–278 (1944).

[24] See R. W. Riemenschneider, J. Turer, and W. C. Ault, Oil & Soap, 21, 98–100 (1944).

[25] S. Musher (to Musher Foundation, Inc.), U. S. Pat. 2,026,697 (1938), and subsequent patents. See also F. N. Peters and S. Musher, Ind. Eng. Chem., 29, 146–151 (1937).

[26] W. G. McLeod, Oil & Soap, 19, 53 (1942).

[27] E. C. Crocker (to Arthur D. Little, Inc.), U. S. Pat. 2,205,620 (1940).

[28] H. T. Spannuth, T. H. McGuine, and G. A. Crapple, Oil & Soap, 23, 110–113 (1946); B. J. Verbeck (to Wilson & Co.), U. S. Pat. 2,354,719 (1944).

[29] G. A. Richardson, M. S. El-Rafey, and M. L. Long, J. Dairy Sci., 30, 397–413 (1947).

[30] S. B. Govindarajan and B. N. Banerjee, Current Sci., 8, 559–560 (1940).

[31] G. S. Fisher, L. Kyame, and W. G. Bickford, J. A. O. C. S., 24, 340–343 (1947).

[32] H. A. Mattill and C. Golumbic (to Lever Bros. Co.), U. S. Pat. 2,233,655 (1943). L. I. Smith and H. E. Ungnade (to the University of Minnesota), U. S. Pat. 2,249,054 (1941).

[33] H. A. Mattill and C. Golumbic (to Lever Bros. Co.), U. S. Pat. 2,233,657 (1943).

and its esters,[34] aldehydic carboxylic acids, such as galacturonic acid,[35] fatty acid monoesters of L-ascorbic and D-isoascorbic acids,[36] dithiodipropionic acids and their esters,[37] and substituted β-mercaptopropionic acids.[38]

Tocopherol concentrates are available from the molecular distillation of vegetable oils or vegetable oil deodorizer sludges, and a material fairly high in tocopherols (*ca.* 0.5%) is obtainable in the form of a special solvent-extracted wheat germ oil.[39] These and other antioxidants derived from edible materials are acceptable lard stabilizers, even though they have not been used a great deal in the past. Aside from tocopherols (up to 0.03%), the only antioxidants that have official Bureau of Animal Industry approval at the present writing (November, 1949) are gum guaiac (up to 0.1%), nordihydroguaiaretic acid (up to 0.01%), propyl gallate (up to 0.01%), thiodipropionic acid (up to 0.01%) or its higher alkyl esters, *e.g.*, dilauryl thiodipropionate (up to 0.09%), butylated hydroxyanisole (up to 0.02%), lecithin (unlimited), and citric or phosphoric acids (up to 0.005%) in combination with any of the preceding.

Gum guaiac,[40-43] a product of the tropical American tree, *Guaiacum officinalis*, was used to the extent of about 0.05% in a popular bland-type lard product for a number of years. By a special technique, involving dissolving the gum in acetic acid[44] and adding the solution to the lard before deodorizing,[45] a tasteless and almost colorless fat was produced with good flavor stability and a keeping quality, by the Swift or A.O.M. method of 20–25 hours, several times that of the original fat. Gum guaiac is not as powerful in its action as some of the more recently developed antioxidants, but it has the considerable advantage of continuing to protect the fat after the latter is incorporated into various baked goods including soda crackers.[43] It has been proved to be completely lacking in toxicity.[46]

[34] L. W. Elder and H. S. Levenson (to General Foods Corp.), U. S. Pat. 2,437,731 (1948).

[35] H. A. Mattill and C. Golumbic (to Lever Bros. Co.), U. S. Pat. 2,233,658 (1943).

[36] R. W. Riemenschneider and J. Turer (to Secretary of Agriculture), U. S. Pat. 2,375,250 (1945). P. A. Wells and R. W. Riemenschneider (to Secretary of Agriculture). U. S. Pat. 2,368,435 (1945).

[37] D. K. O'Leary (to E. I. du Pont de Nemours & Co.), U. S. Pat. 2,397,976 (1946).

[38] M. F. Gribbins, F. W. Miller, Jr., and D. K. O'Leary (to E. I. du Pont de Nemours & Co.), U. S. Pat. 2,397,960 (1946).

[39] A. Lips and W. D. McFarlane, *Oil & Soap, 20*, 193–196 (1943).

[40] D. P. Grettie, *Oil & Soap, 10*, 126–127 (1933).

[41] H. S. Mitchell and H. C. Black, *Ind. Eng. Chem., 35*, 50–52 (1943).

[42] R. C. Newton and D. P. Grettie (to Swift & Co.), U. S. Pat. 1,903,126 (1933).

[43] J. W. Higgins and H. C. Black, *Oil & Soap, 21*, 277–279 (1944).

[44] J. L. Doegey (to Industrial Patents Corp.), U. S. Pat. 2,308,912 (1943).

[45] G. W. Phelps and H. C. Black (to Industrial Patents Corp.), U. S. Pat. 2,374,234 (1945).

[46] V. Johnson, J. Carlson, N. Kleitman, and P. Bergstrom, *Food Research, 3*, 555–574 (1938).

Another substance of plant origin that has found considerable use as a lard antioxidant is nordihydroguaiaretic acid (NDGA):[47]

$$\text{HO}—\langle\text{ring}\rangle—\text{CH}_2.\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{CH}_2—\langle\text{ring}\rangle—\text{OH}$$

(HO, HO on left ring; OH, OH on right ring)

which is extracted from the common American desert plant, *Larrea divaricata*, or creosote bush.[48] This antioxidant, in a concentration of 0.01% or less, extends the keeping time remarkably; its principal disadvantage for some purposes is a relatively poor carryover into baked goods.

The lower alkyl gallates, and particularly propyl gallate,[49] are highly effective antioxidants and have the advantage over NDGA of being somewhat more easily soluble in fat. Propyl gallate does not give good protection to lard in baked goods, nor do higher alkyl gallates.[50]

The latest synthetic antioxidant to be approved for lard is butylated hydroxyanisole (BHA),[51] a mixture of the two isomers:

OCH₃ with C(CH₃)₃ and OH; OCH₃ with C(CH₃)₃ and OH

$$\text{OCH}_3 \quad \text{C(CH}_3)_3 \quad \text{OH} \qquad \text{OCH}_3 \quad \text{C(CH}_3)_3 \quad \text{OH}$$
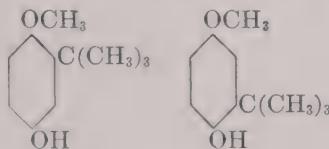
This appears to be the long-awaited "ideal" synthetic antioxidant, which combines to a high degree the properties of nontoxicity, stability, freedom from color and flavor, fat solubility, water insolubility, and effectiveness both in pure fats and in baked goods. Although but recently approved by the B.A.I., it has attained wide popularity.

All antioxidants of the phenolic type, including the four mentioned above, are reinforced by the presence of certain acidic "synergists." The effective synergists include, among many others, commercial lecithin and citric and phosphoric acids. One of these is usually used in combination with the phenolic inhibitors. Butylated hydroxyanisole is preferably used in synergistic combination with propyl gallate and citric or phosphoric acid.

Representative keeping quality tests reported by different workers on lard, with and without certain of the more popular antioxidants and synergists, are shown in Table 65. It is to be noted that this table indicates

[47] W. O. Lundberg, H. O. Halvorson, and G. O. Burr, *Oil & Soap*, *21*, 33–35 (1944). W. M. Lauer (to Secretary of Agriculture), U. S. Pat. 2,373,192 (1945).

[48] A. Fonyo, *Oil & Soap*, *23*, 75–77 (1946).

[49] T. Sabalitschka and E. Bohn (to Heyden Chem. Corp.), U. S. Pat. 2,255,191 (1941).

[50] S. G. Morris and R. W. Riemenschneider, *J. Am. Oil Chem. Soc.*, *26*, 638–640 (1949).

[51] H. R. Kraybill, L. R. Dugan, Jr., B. W. Beadle, F. C. Vibrans, V. Swartz, and H. Rezabek, *J. Am. Oil Chem. Soc.*, *26*, 449–453 (1949).

only the probable effect of different antioxidants upon the shelf life of lard, and gives no information relative to the carryover of antioxidant activity into the fat in baked goods.

TABLE 65

EFFECT OF DIFFERENT ANTIOXIDANTS ON KEEPING QUALITY OF LARD AS MEASURED BY A.O.M. TEST

Antioxidant	Amount, %	K. Q., hrs. Unprotected	K. Q., hrs. Protected	Antioxidant	Amount, %	K. Q., hrs. Unprotected	K. Q., hrs. Protected
α-Tocopherol[a]	0.10	10	17	Gum guaiac[d]	0.05	6	20
β-Tocopherol[a]	0.10	10	22	NDGA[d]	0.01	5	18
γ-Tocopherol[a]	0.10	10	35	NDGA[g]	0.01	3	25
δ-Tocopherol[a]	0.10	10	42	NDGA[h]	0.01	11	210
α-Tocopherol[b]	0.03	5.0	21	Propyl gallate[d]	0.01	6	33
γ-Tocopherol[b]	0.03	5.0	35	Propyl gallate[i]	0.01	7	70
Mixed cottonseed oil tocopherols[b]	0.03	5.0	20	Dodecyl gallate[i]	0.02	7	70
Mixed peanut oil tocopherols[c]	0.03	5.0	28	Gallic acid[i]	0.01	7	66
Vegetable oil tocopherols[d]	0.02	4.0	16	Tannic acid[i]	0.10	6	37
Refined corn oil[e]	2.5	6.0	15.0	Norconidendrin[g]	0.01	3	22
Refined soybean oil[e]	2.5	6.0	14.0	BHA[k]	0.01	4	21
Refined cottonseed oil[e]	2.5	6.0	11.5	BHA plus 0.003% propyl gallate and 0.002% citric acid[k]	0.01	4	60
Wheat germ oil plus citric acid[f]	0.2	2.5	5.4				

[a] J. Griewahn and B. F. Daubert, *J. Am. Oil Chem. Soc.*, *25*, 26–27 (1948).
[b] W. S. Singleton and A. E. Bailey, *Oil & Soap*, *21*, 224–226 (1944).
[c] G. D. Oliver, W. S. Singleton, and A. E. Bailey, *Oil & Soap*, *21*, 188–193 (1944).
[d] J. W. Higgins and H. C. Black, *Oil & Soap*, *21*, 277–279 (1944).
[e] R. W. Riemenschneider, J. Turer, and W. C. Ault, *Oil & Soap*, *21*, 98–100 (1944).
[f] A. Lips and W. D. McFarlane, *Oil & Soap*, *20*, 193–196 (1943).
[g] G. S. Fisher, L. Kyame, and W. G. Bickford, *J. Am. Oil Chem. Soc.*, *24*, 340–343 (1947).
[h] W. O. Lundberg, H. O. Halvorson, and G. O. Burr, *Oil & Soap*, *21*, 33–35 (1944).
[i] S. G. Morris, L. A. Kraekel, D. Hammer, J. S. Meyers, and R. W. Riemenschneider, *J. Am. Oil Chem. Soc.*, *24*, 309–311 (1947).
[j] H. T. Spannuth, T. H. McGuine, and G. A. Crapple, *Oil & Soap*, *23*, 110–113 (1946).
[k] H. R. Kraybill, L. R. Dugan, Jr., B. W. Beadle, F. C. Vibrans, V. Swartz, and H. Rezabek, *J. Am. Oil Chem. Soc.*, *26*, 449–453 (1949).
Note: In a few cases, where the A.O.M. test was conducted at 110 °C. instead of the standard temperature of 97.8 °C., the stability values reported have been multiplied by a factor of 2.5, to make them comparable with other values in the table (see Chapter II).

6. DEODORIZED LARD PRODUCTS

There is a relatively small but growing production of shortening products which consists of lard that has been stiffened by hydrogenation or the addition of hard fats, deodorized, and fortified with antioxidants.

One popular product,[41,42] which has been on the market for some years in household packages, is stiffened with hydrogenated lard and protected from oxidation by the addition of citric acid and gum guaiac (or more recently, propyl gallate). Recently, it has been converted to a so-called "high-ratio" shortening by the inclusion of mono- and diglycerides. Another relatively old product consists of an all-hydrogenated lard,[52] with an iodine value of 58–62. Lard products of this class have found particular favor with certain deep fryers of food products. A recently introduced animal fat shortening consists of a blend of lard with beef fat and highly hydrogenated lard, deodorized, and fortified with propyl gallate and lecithin.[53]

Generally, in the manufacture of these so-called bland-type lard products the processing steps are similar to those applied to crude vegetable oils for the manufacture of vegetable shortenings except that alkali refining is omitted and efficient steam stripping in the deodorizer is depended upon to reduce the free fatty acid content of the fat from 0.30–0.40% to 0.01–0.03%.[53]

7. RENDERED PORK FAT

Since 1940, regulations of the U. S. Department of Agriculture have provided that the fat rendered from certain low grade stocks shall not be labeled and sold as lard, but must be designated "rendered pork fat." The regulations of the Bureau of Animal Industry which define lard and rendered pork fat are as follows:

Lard. The fat rendered from fresh, clean, sound fatty tissues from hogs in good health at the time of slaughter, with or without lard stearine or hardened lard. The tissues do not include bones, detached skin, head fat, ears, tails, organs, windpipes, large blood vessels, scrap fat, skimmings, settlings, pressings and the like, and are reasonably free from muscle tissue and blood.

Rendered pork fat. The fat other than lard, rendered from clean, sound carcasses, parts of carcasses, or edible organs from hogs in good health at the time of slaughter, except that stomachs, tails, bones from the head and bones from cured or cooked pork are not included. The tissues rendered are usually fresh, but may be cured, cooked, or otherwise prepared and may contain some meat food products. Rendered pork fat may be hardened by the use of lard stearine and/or hardened lard and/or rendered pork fat stearine and/or hardened rendered pork fat.

The production of rendered pork fat amounts usually to about 10% of the total amount of hog fat rendered in government-inspected establishments. Rendered pork fat has been included with lard in the statistics previously quoted on the production of lard.

[52] J. R. Shipner (to Cudahy Packing Co.), U. S. Pat. 1,755,135 (1930).
[53] A. E. Bailey, *Natl. Provisioner, 119,* No. 18, 10–11, 23 (October 30, 1948).

Whereas the aforementioned regulations were set up with the object of improving lard quality, it is to be noted that rendered pork fat is not necessarily inferior to lard except in its relatively dark color and somewhat more pronounced flavor. The stability of rendered pork fat is, in fact, often superior to that of lard.

8. PLASTIC OLEO OIL

A small amount of oleo oil of both extra and prime grades is converted to a plastic product by solidification in equipment similar to that used for lard and shortenings. The solidified product is packed in drums and sold to the bakery and confectionery trade. It is only suitable for certain specialty uses, and is not packaged for household consumption. Oleo oil is not a good shortening for general use because of its rather limited plastic range.

Plastic oleo oils are often stabilized by the addition of approximately 0.1% of soybean lecithin. Lecithin is a very effective antioxidant for oleo oil. The addition of 0.1% will increase the stability of this product from 8 to 15 hours to about 60 hours, as measured by the Swift method. The stabilizing effect of the lecithin is lost, however, after the fat is baked into crackers, cookies, etc.

D. Shortenings

1. TYPES OF SHORTENING

Shortenings, as manufactured in the United States, fall into two more or less distinct classes, *i.e.*, those of the *compound* or *blended* type and those of the *all-hydrogenated type*. Compound-type shortenings may be further divided into *animal and vegetable* fat compounds and *all-vegetable* compounds. All-hydrogenated shortenings may be subdivided into *regular* or *general purpose* shortenings, *biscuit and cracker type* shortenings, and *superglycerinated* shortenings.

In the earlier days of shortening manufacture, there was a distinct difference in composition between products of the compounded and all-hydrogenated types. Where hydrogenation was used in the preparation of compounds, the invariable practice was to hydrogenate highly a minimum proportion of oil and blend this with untreated oil. Now it is common practice to blend highly hydrogenated oil with slightly hydrogenated oil or even to blend three or more fats or oils, all of which have been hydrogenated to different degrees. Thus, insofar as the composition of the products is concerned, the distinction between compounds and all-hydrogenated shortenings is no longer clear cut. However, the two products continue to be differentiated by other characteristics. All-hydrogenated shortenings are more carefully and thoroughly refined and deodorized, and are of

generally higher quality than compounds. They sell at a price substantially above that of compound shortenings. In some respects all-hydrogenated shortenings are superior to compounded shortenings principally because of the increased care customarily taken in their manufacture. In several important particulars, however, all-hydrogenated shortenings and shortenings of the true compound type are fundamentally different.

All-hydrogenated shortenings are naturally more stable than compounded or blended shortenings. Most compounded shortenings contain from 80 to 90% of highly unsaturated oil. The addition of 10 to 20% of hard fat to the oil does not produce a mixture with either its unsaturation or stability greatly improved over that of the original oil. Many compounds have an iodine value of about 90 and contain 40% or more of linoleic acid. The keeping quality, by the Swift method, of a compound made with cottonseed oil, is about 16 to 18 hours, as compared with about 12 to 16 hours for the original oil.
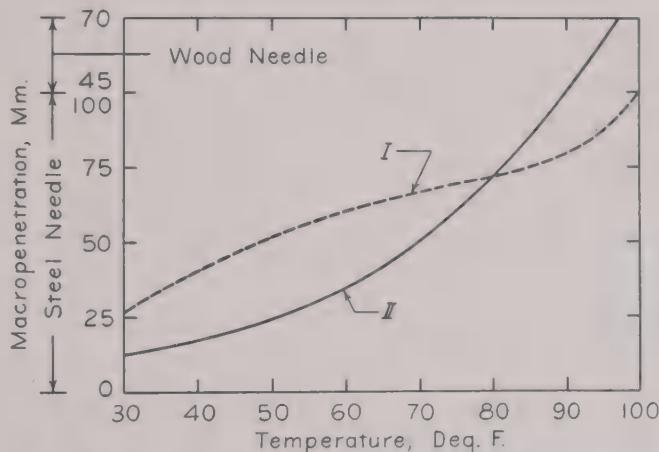
Fig. 24. Macropenetration curves of typical samples of: (I) blended shortening, and (II) all-hydrogenated shortening.

In contrast to the compounds, an all-hydrogenated shortening will usually have an iodine value of 65–75, and a linoleic acid content not greater than 5 to 10%. The Swift keeping time of such a shortening will be not less than 70 hours. The disparity in keeping quality between the two types of shortening is accentuated by the customary practice of packing compounds for household use in cartons and other unsealed containers and packing similar all-hydrogenated shortenings in airtight cans or jars.

The second fundamental point of difference between the two types of shortening is in their plastic range and their change in consistency with variations in temperature. Compound-type shortenings naturally have a longer plastic range than all-hydrogenated shortenings, and are both

softer at low temperatures and firmer at high temperatures. The differ-
ence in this respect between representative samples of the two types is
shown graphically in Figure 24.

The range of macropenetrations within which a shortening is at the best
consistency for working and mixing is about 40 to 90 mm. It will be seen
that a typical compounded shortening is within this range of penetrations
between about 45 and 104°F. A typical all-hydrogenated shortening will
have the same consistency only within the more restricted range of about
64 to 87°F.

Biscuit- and cracker-type shortenings (which are often also used for
commercial frying) and superglycerinated shortenings are modified forms
of the regular all-hydrogenated type. They have been developed to meet
the specialized requirements of commercial bakers for products with high
stability and strong emulsifying properties, respectively.

2. Raw Materials

Since a suitable consistency in shortening may be obtained both by
blending hard and soft fats and by hydrogenating soft fats, a very wide
variety of oils may be used in the manufacture of this product.

Oleostearine and edible tallow are the two natural hard fats most widely
used in shortening manufacture. The proper percentages of these fats
for stiffening a liquid oil are about 20 and 50%, respectively. It is com-
mon, however, to use somewhat less tallow (25 to 40%) and obtain an
additional stiffening effect by hydrogenation, or the addition of hydro-
genated vegetable stearine. A considerable amount of lard and rendered
pork fat goes into shortenings.

Cottonseed oil, peanut oil, sunflowerseed oil, corn oil, and sesame oil
are suitable ingredients for compounded shortenings without being hydro-
genated. Soybean, fish, and whale oils are customarily hydrogenated con-
siderably before being incorporated into shortenings, in order to minimize
their tendency to flavor reversion. Fish oil is used only in the cheaper
grades of shortening.

High-grade all-hydrogenated shortenings are made principally from
cottonseed, soybean, and peanut oils. Cottonseed and peanut oils may be
used freely and interchangeably. It is preferable to use not more than
about 30% of soybean oil in this type of shortening because of its flavor
reversion and its disagreeable odor at frying temperatures; however, it is
not always possible to keep the soybean oil content this low. Fish oil,
whale oil, rapeseed oil, or other oils containing highly unsaturated acids
are used very sparingly, or not at all. Palm oil is a suitable ingredient for
either type of shortening, but is usually subjected to some degree of
hydrogenation, because of its dark color and the pronounced bleaching
effect of this process.

Coconut oil and other lauric acid oils are not among the more desirable materials for shortening manufacture, because of their short plastic range and their tendency to foam when used for deep frying.

The fats and oils used in the manufacture of all classes of shortenings in the United States in recent years are listed in Table 66. In the United Kingdom, cottonseed oil, whale oil, and peanut oil comprise the principal materials used in shortenings; very little shortening containing animal fats is manufactured. The principal shortening oils in Russia are sun-flowerseed, cottonseed, and linseed oil.

TABLE 66

FATS AND OILS USED IN MANUFACTURE OF SHORTENING IN UNITED STATES
(MILLIONS OF POUNDS)[a]

Fat	Average 1937–41	1946	1947	1948
Babassu oil	0.4	2.9	0.7	[b]
Coconut oil	19.8	17.8	86.5	48.3
Corn oil	0.9	3.3	2.6	3.7
Cottonseed oil	966.2	501.6	299.9	321.1
Fish oils	15.1	1.2	—	—
Lard and rendered pork fat	15.7	20.4	100.6	114.0
Oleo oil	0.6	1.4	1.5	0.6
Oleostearine	25.6	13.2	18.9	14.5
Palm oil	94.3	—	—	2.9
Peanut oil	53.3	42.3	64.5	55.9
Sesame oil	7.1	—	—	2.1
Soybean oil	171.6	743.5	705.3	707.5
Tallow, edible	55.6	43.8	44.5	29.2
Vegetable oil stearine	[d]	69.4	69.6	100.6
Other oils	2.3	5.0	1.2	2.1
Total	1428.6	1465.8	1395.8	1402.5

[a] Bureau of Agricultural Economics, U. S. Dept. Agr., *The Fats and Oils Situation*, July-August, 1950. Figures are for primary fats and oils only.
[b] Included in "Other oils."
[c] From winterizing. Largely cottonseed.
[d] Included in cottonseed oil, etc.

3. COMPOUNDS OR BLENDED SHORTENINGS

(a) Animal and Vegetable Compounds

In the United States, there is a rather sharp distinction between compounds containing both animal and vegetable fats and those made exclusively from vegetable oils, because of the necessity for the former to be made under inspection of the Bureau of Animal Industry of the Department of Agriculture. Practically all of the animal and vegetable compounds are manufactured by meat-packing companies. Although compounds of this class originally constituted the whole of the United States'

TABLE 67

VARIATIONS IN HARDNESS AND UNSATURATION OF EDIBLE TALLOW FROM
VARIETY OF SOURCES

Source	Iodine value	Micropen., mm./10 at 70°F.
U. S., Omaha, Nebraska.............	47	31
U. S., Omaha, Nebraska.............	42	23
U. S., St. Paul, Minnesota...........	40	20
U. S., St. Paul, Minnesota...........	40	21
U. S., Sioux City, Iowa..............	43	27
U. S., Sioux City, Iowa..............	41	23
U. S., Atlanta, Georgia..............	37	17
U. S., Camden, New Jersey..........	51	41
Argentina........................	42	21
Argentina........................	49	38
Uruguay.........................	47	31
Paraguay........................	48	30
Paraguay........................	44	27
New Zealand.....................	42	25
Australia........................	40	21
Australia........................	41	24

TABLE 68

CONSISTENCY CHARACTERISTICS OF TYPICAL COMPOUND-TYPE SHORTENINGS IN
COMPARISON WITH TYPICAL ALL-HYDROGENATED SHORTENING

Constituents	Extent hydrog.[a]	Iodine value	Macropenetration at temp., °F. indicated[b]				
			50	70	80	90	95
20% oleostearine, 80% cottonseed oil.........	0	91	40	60	68	75	82
55% tallow, 45% cotton oil................	0	72	30	55	70	90	50[f]
5% stearine,[c] 45% tallow, 50% cotton oil.....	2	72	28	50	60	73	85
5% stearine,[d] 35% tallow, 60% cotton oil.....	6	78	31	53	64	79	99
5% stearine,[d] 15% tallow, 60% lard, 20% cotton oil................	4	65	28	55	70	80	90
12% stearine,[d] 88% cotton oil..............	0	97	48	65	74	78	82
10% stearine,[d] 90% cotton oil..............	6	92	44	63	73	79	84
5% stearine,[d] 35% hydrog. soybean oil,[e] 60% cotton oil................	6	76	32	55	68	85	96
5% stearine,[d] 95% cotton oil..............	38	65	24	50	64	88	55[f]

[a] Decrease in iodine value of the mixture upon hydrogenation.
[b] In terms of millimeters with the Goddard-Hewes penetrometer, steel needle unless otherwise indicated.
[c] Hydrogenated tallow, titer = 57°.
[d] Hydrogenated vegetable oil, titer = 59°C.
[e] Iodine value = 55.
[f] Wood needle.

shortening production, they have been decreasing in importance for a number of years, and are now much exceeded in volume by vegetable shortenings.

Only a small proportion of the animal and vegetable shortening produced at present is made to the original formula of approximately 20% oleostearine and 80% cottonseed oil (or other vegetable oil). A considerable amount is made from vegetable oil and tallow, with an average tallow content in the neighborhood of perhaps 35%. Most of the shortening containing tallow is either stiffened by slight hydrogenation, or stiffened by the adition of a small proportion (e.g., 5%) of hydrogenated stearine.

In shortenings containing either tallow or oleostearine, any desired proportion of the beef fat–vegetable oil blend may be substituted with lard, or lard may be blended with vegetable oil and a small percentage of hydrogenated animal or vegetable stearine.

The over-all quality, and particularly the flavor stability of a blended animal and vegetable shortening, is greatly improved if the blend is subjected to slight hydrogenation, e.g., to reduce the iodine value 2–10 units.

Slight hydrogenation of a mixture of 20% oleostearine and 80% cottonseed oil has the effect of softening the mixture in the range of about 90° to 100°F., rather than stiffening it, as might be expected. The following is a typical series of variations in the 98°F. macropenetrations of such a mixture, hydrogenated to different degrees:

Unhydrogenated mixture.......................... 42 mm. (wood needle)
Iodine value reduced 4 units...................... 48 mm.
Iodine value reduced 6 units...................... 52 mm.
Iodine value reduced 8 units...................... 58 mm.
Iodine value reduced 14 units.................... 52 mm.

A similar effect is noted in hydrogenating a mixture of hydrogenated vegetable stearine (iodine value 10–15) and cottonseed oil. However, the addition of a small amount of stearine to vegetable oil which is to be made into all-hydrogenated vegetable shortening will improve the 98°F. body of the product, and 3 to 5% is often used for this purpose.

If much tallow is to be used in a blended shortening formula, with or without slight hydrogenation, it is impossible to maintain the proportion of tallow constant and at the same time turn out a product of uniform consistency. This is because there are considerable variations in the hardness of different lots of commercial edible tallow. In Table 67 are some micropenetrations of different shipments of edible tallow, from various sources.

Since tallow has become an important ingredient of animal and vegetable shortenings, and cottonseed oil has been supplemented by large supplies of soybean and other vegetable oils, the blending of compound shortenings has become a somewhat involved matter. Obviously, an al-

most infinite variety of blends are possible. The penetration data in Table 68 furnish an idea of the consistency characteristics of different blends, in comparison with a typical all-hydrogenated shortening.

The analysis given by Black[53a] for typical samples of animal and vegetable compound shortenings are shown in Table 69.

Probably a greater proportion of the total production goes into household packages than is the case with either all-vegetable compounds or all-hydrogenated shortenings.

TABLE 69

CHARACTERISTICS OF TYPICAL COMPOUND-TYPE SHORTENINGS[a]

Constituents...............	20% Oleostearine 20% Lard 20% Tallow 40% Cottonseed oil	10% Stearine[b] 10% Oleostearine 20% Soybean oil 60% Cottonseed oil	10% Stearine[c] 40% Hydrog. soy- bean oil 50% Cottonseed oil
Iodine value...............	75.5	95.5	90.2
Free fatty acids, %.........	0.10	0.10	0.10
Color (Lovibond)...........	20 Y–1.2 R	20 Y–2.0 R	20 Y–2.0 R
Stability, A.O.M., hrs.......	20	25	30
Smoke point, °F............	400	400	400
Flavor....................	Bland	Bland	Bland

[a] H. C. Black, in A. E. Bailey, ed., *Cottonseed and Cottonseed Products*, Interscience, New York, 1948, pp. 743–744.
[b] Hydrogenated cottonseed oil.
[c] Hydrogenated soybean oil.

(b) All-Vegetable Compounds

All-vegetable compounds are similar in composition to animal and vegetable compounds, with the exception that highly hydrogenated vegetable oils are substituted for the hard animal fats which are used in the latter class of products.

If an all-vegetable shortening is to be made with a minimum amount of hardened oil, the latter is usually hydrogenated to an iodine value of 15 or less. In the case of a shortening which is to be made with a liquid oil, about 10 to 15% of hardened oil or vegetable stearine is required in the mixture, the exact amount depending upon the iodine value and titer of the stearine and the consistency desired. If a partially hydrogenated soft oil is to be used, slightly less may be required. The consistency of all-vegetable compounds is quite similar at all temperatures to that of an animal and vegetable compound containing oleostearine (see Table 68).

If soybean oil or other oil which is inclined to revert in flavor is to be used in limited quantities in a compounded shortening, it is usually desir-

[53a] H. C. Black, Chapter XVIII in *Cottonseed and Cottonseed Products*, A. E. Bailey, ed., Interscience, New York, 1948.

able to hydrogenate this oil as much as is possible. In such a case, the more unstable oil may be hydrogenated to the approximate consistency of tallow and blended with cottonseed, peanut, or other more stable oils in the same proportions in which tallow is used in animal and vegetable compounds. A similar procedure is desirable when whale or fish oils are to be used in shortenings of this type. Hydrogenation may, in fact, be considered very nearly as essential in the manufacture of blended shortenings as in the production of those of the all-hydrogenated type. It is possible, of course, for a manufacturer to produce a blended shortening without the benefit of hydrogenation facilities, but in so doing he is severely limited in his choice of raw materials.

Coconut oil, as stated previously, yields a shortening of rather poor plastic range. If coconut oil is to be used in a shortening in large proportions, the product is best made by blending unhydrogenated coconut oil with about 8 to 12% of vegetable stearine and as much cottonseed oil or other liquid oil as may be permissible to use. Highly hydrogenated coconut oil has a melting point of only about 110°F., hence vegetable stearine cannot be made from this oil.

Most of the all-vegetable shortening manufactured in the United States is prepared from cottonseed, soybean, and peanut oils, although if available, corn, palm, sesame, or sunflower oils are entirely suitable materials.

The analysis of a typical all-vegetable compound is shown in Table 69.

Statistical data on the annual production of shortenings according to classes, *i.e.*, animal and vegetable compounds, all-vegetable compounds, and all-hydrogenated vegetable shortenings, are not available. However, the U. S. Census of Manufactures showed a factory production of 410 million pounds of animal and vegetable shortening and 986 million pounds of vegetable shortening in 1947, and 351 million pounds of animal and vegetable shortening and 1030 million pounds of vegetable shortening in 1939.

4. ALL-HYDROGENATED SHORTENINGS

The production of all-hydrogenated shortenings in the United States has for some time been steadily increasing, both in actual volume and in relation to the total shortening manufactured. At the present time more than one-half the total shortening manufactured is of this type.

All-hydrogenated shortening is used to the near exclusion of all other fats by commercial bakers for making certain products, such as cakes and cookies. It is also widely used in almost every other variety of baked product, and is popular with restaurants and hotels, and commercial deep fryers. Large quantities are also consumed in home cooking, although the proportion so consumed is less than that of the blended shortenings. For

commercial use, all-hydrogenated shortening is packed in the usual drums and cans, but for household consumption it is put up in sealed 1- or 3-pound cans or jars.

Although minor quantities of peanut oil, corn oil, sesame oil, sunflower-seed oil, palm oil, etc., go into the making of this class of shortening, present technology in the United States is based primarily upon the use of cottonseed and soybean oils. Except where otherwise stated, the following discussion will apply to the use of these two oils.

(a) Hydrogenation and Blending

Except for certain special products of high stability, prepared for commercial deep frying or biscuit and cracker making, all-hydrogenated shortenings are almost invariably made by blending 3–5% of very highly hydrogenated oil ("flakes," hard oil, or stearine) with oil partially hydrogenated, i.e., to within the range of about 65–80 iodine value. The partially hydrogenated or soft stock may consist of a single oil or a blend of oils which has been hydrogenated to a specific consistency. More commonly, however, two soft or base stocks are used, one of which is somewhat harder than the other. This method has the advantage of not requiring such careful control of the hydrogenation process, inasmuch as the consistency of the product can be controlled within certain limits by varying the proportions of the two soft stocks. Furthermore, it permits soybean oil or other oil of relatively poor flavor stability to be hydrogenated to a greater degree than cottonseed oil or other more stable oils. However, the double soft base stock method does not produce a shortening quite as low in iodine value or of as good keeping quality as the single base stock method.

The various analytical methods for controlling the consistency of hydrogenated stocks will be discussed in a later chapter (Chapter XVII). Of the characteristics useful for control purposes the so-called *setting point* or *congeal point* (page 753) is probably the most commonly used; in the hydrogenation of shortening stocks the object is to bring the oil to the desired congeal point at the lowest possible iodine value.

If a single base stock is to be blended with 5% of hard oil (titer, 61–63°C.), it is usually hydrogenated to a congeal point of about 26.0°C., to give a finished product with a congeal point of about 32.5°C. and a Wiley melting point in the neighborhood of 41°C. Innumerable combinations are possible with two base stocks. One popular method involves blending about 5% hard stock with about 20% base stock hardened to a congeal point of *ca.* 38.0°C., adding about 75% base stock hardened to *ca.* 24.0°C.

congeal point. A product is obtained with a congeal point of about 32.0°C.
and a Wiley melting point of 40–41°C.

Whereas a small percentage of a highly hydrogenated fat is customarily
added to shortenings to provide a stiffening effect at higher temperatures,
it is by no means essential that this be done. It is possible to produce
enough highly saturated glycerides to provide good high temperature body
in the course of partial hydrogenation, thus avoiding the blending of hard
and soft stocks altogether. The nonselective hydrogenation that is required
is somewhat difficult, however, since high pressures and low temperatures
must be employed, and the blending method is generally preferred.

(b) Consistency of the Product vs. Selectivity[54] in Hydrogenation

Hydrogenation causes fats to become firmer both by decreasing the
unsaturation of the component fatty acids and by converting unsaturated

TABLE 70

COMPOSITION AND CHARACTERISTICS OF COTTONSEED OIL[a] HYDROGENATED WITH
VARYING DEGREES OF SELECTIVITY

Selectivity	Iodine value	Micropen. at 22.5°C.	Fatty acids, %			
			Sat.	Iso-oleic	Oleic	Linol.
Very selective[b]..........	67.2	65	27.8	18.9	47.6	5.7
	62.3	40	28.4	23.7	47.0	0.9
	58.6	20	30.8	26.6	42.6	0.0
	(63.6)[e]	45	28.2	22.3	47.3	2.2
Moderately selective[c].....	69.4	130	28.3	9.9	52.9	8.9
	64.2	90	29.8	11.0	55.1	4.1
	58.2	50	32.8	11.7	55.1	0.4
	(63.6)[e]	86	30.2	11.1	54.6	4.1
Nonselective[d]...........	70.8	120	33.2	6.5	45.6	14.7
	66.7	80	34.2	6.9	47.4	11.5
	59.9	45	36.9	6.9	49.4	7.1
	(63.6)[e]	62	35.2	6.8	49.0	9.0

[a] Composition of original oil: saturated acids, 26.0%; iso-oleic, 1.1%; oleic, 27.6%;
inoleic, 45.3%. All analyses by Twitchell lead soap–alcohol method.

[b] Hydrogenation conditions: 350°F., 60 p.s.i.g. pressure, low agitation, 0.10% nickel,
15-lb. batch in laboratory dead-end convertor.

[c] Hydrogenation conditions: 350°F., 60 p.s.i.g. pressure, medium agitation, 0.10%
nickel, 15-lb. batch in laboratory dead-end convertor.

[d] Hydrogenation conditions: 225°F., 60 p.s.i.g. pressure, high agitation, 0.10%
nickel, 15-lb. batch in laboratory dead-end convertor.

[e] Interpolated values. Iodine value of 63.6 corresponds to iodine value of oil hydro-
genated with perfect selectivity, i.e., with 26.0% saturated acids, 74.0% oleic acids.

[54] The term "selectivity" is used here in reference to the preferential saturation
of polyethenoid acids in the presence of oleic acid, rather than in the colloquial
sense of attaining the proper consistency in the fat at a minimum iodine value.

acids to higher melting isomers, *i.e.*, by forming "iso-oleic" acids.[54a]

In considering the degree to which each of these effects contribute to hardening it will be convenient to refer to the tabulations of analytical

TABLE 71

COMPOSITION AND CHARACTERISTICS OF SOYBEAN OIL[a] HYDROGENATED SELECTIVELY AND NONSELECTIVELY

Selectivity	Iodine value	Micropen. at 22.5°C.	Fatty acids, %	
			Saturated	Iso-oleic
Moderately selective[b]......	84.2	130	19.5	21.9
	79.2	100	20.2	21.4
	74.3	60	22.4	23.7
	68.9	30	25.2	27.0
	65.5	25	27.2	28.4
	(74.5)[f]	60	22.4	23.7
Moderately selective[c]......	84.7	190	17.9	15.7
	77.8	130	20.1	17.6
	72.2	70	22.7	20.0
	66.3	40	27.0	18.5
	58.4	25	34.1	19.4
	(74.5)[f]	85	21.9	18.8
Nonselective[d]............	82.0	75	23.6	16.0
	74.5	40	26.8	18.2
	67.0	25	30.9	21.1
	61.3	20	34.4	21.8
	(74.5)[f]	40	26.8	18.2
Nonselective[e]............	84.0	140	22.2	9.1
	80.1	100	23.6	10.3
	74.7	70	25.6	11.1
	68.1	40	29.0	10.9
	62.6	30	33.1	10.9
	(74.5)[f]	70	25.6	11.1

[a] Composition of original oil: saturated acids, 13.4%; iso-oleic acids, 2.2%. All analyses by Twitchell lead soap–alcohol method.

[b] Hydrogenation conditions: 375°F., 5 p.s.i.g. pressure, high agitation, 0.03% nickel, 15-lb. batch in laboratory dead-end convertor.

[c] Hydrogenation conditions: 275°F., 5 p.s.i.g. pressure, high agitation, 0.15% nickel, 15-lb. batch in laboratory dead-end convertor.

[d] Hydrogenation conditions: 375°F., 60 p.s.i.g. pressure, high agitation, 0.02% nickel, 15-lb. batch in laboratory dead-end convertor.

[e] Hydrogenation conditions: 275°F., 60 p.s.i.g. pressure, high agitation, 0.05% nickel, 15-lb. batch in laboratory dead-end convertor.

[f] Interpolated values. Iodine value of 74.5 corresponds to iodine value of oil hydrogenated with perfect selectivity, *i.e.*, with 13.4% saturated acids, 86.6% oleic acids.

Note: The results in this table and in Table 70 are not strictly comparable, as different catalysts were used for the two series of tests.

data for cottonseed oil hydrogenated in the laboratory under very selective, moderately selective, and nonselective conditions, in Table 70, and

[54a] It should be recognized that the content of "iso-oleic" acids has only a relative significance, inasmuch as the analytical method obviously detects only a portion of the total isomers.
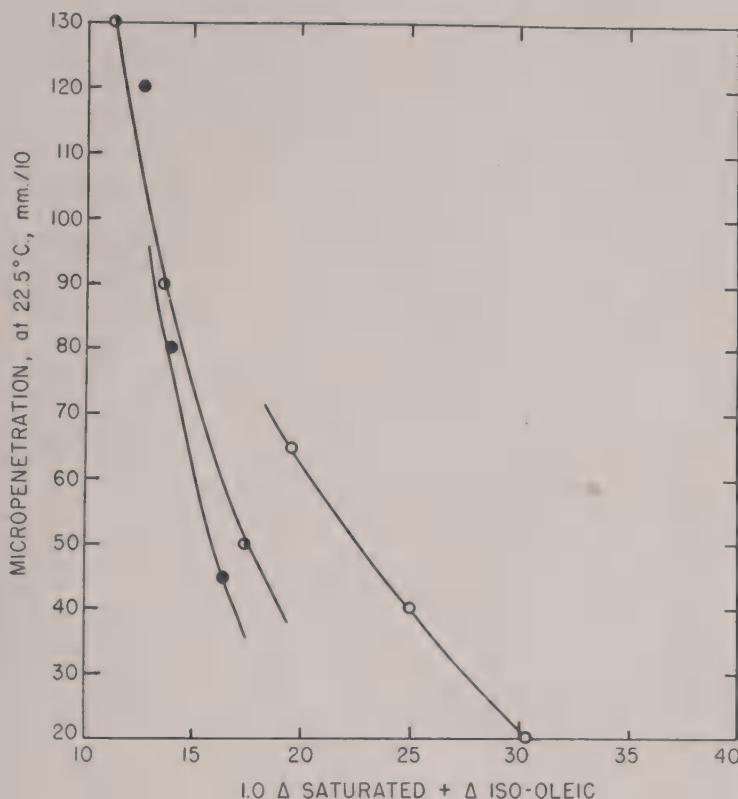
Fig. 25. Consistency of hydrogenated cottonseed oil at 22.5°C. in relation to saturated and iso-oleic acids formed during hydrogenation: saturated acids and iso-oleic acids given equal weight. (Open circles represent samples from highly selective hydrogenation; half-closed circles represent samples from moderately selective hydrogenation; closed circles represent samples from nonselective hydrogenation.)

to the corresponding data for selectively and nonselectively hydrogen-ated soybean oil in Table 71.

In view of the fact that pure elaidic acid melts somewhat above 40°C., it is logical to expect that iso-oleic acids as well as saturated acids would contribute to stiffening of a hydrogenated fat at 70–75°F., and inspection of Tables 70 and 71 will reveal that such is indeed the case.[55] It is evident, however, that the saturated and the iso-oleic acids produced in cottonseed oil by hydrogenation do not stiffen the fat equally. If the two are given equal weight and the combined percentage is plotted against the micropenetration at 22.5°C., as in Figure 25 the points representing the selectively hydrogenated samples (low saturated acids, high iso-oleic acids) fall to the right of the chart, and the points representing non-

[55] That iso-oleic acids contribute largely to the body of a fat at 70–75°F., but little to the high temperature body, is a matter of common knowledge among practi-cal hydrogenators of shortening and margarine oils.

selective hydrogenation fall to the left, indicating that too little relative weight has been given to the saturated acids and too much weight has been given to the iso-oleic acids. If the composite figure for the two acids is weighted 2 to 1 in favor of the saturated acids, i.e., if this figure is taken as twice the saturated acids plus the iso-oleic acids, as in Figure 26, the points for very selective and for moderately selective hydrogenation fall in line (on the broken curve in the figure), but the points for nonselective hydrogenation fall to the right, indicating that too much weight has been given to the saturated acids. The best fit for all data is obtained with
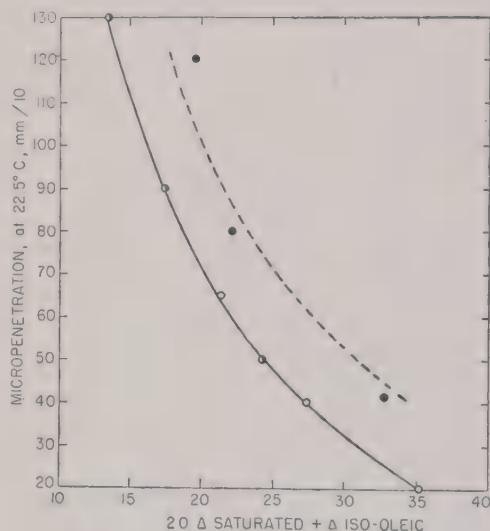
Fig. 26. Consistency of hydrogenated cottonseed oil at 22.5°C. in relation to amount of saturated and iso-oleic acids formed during hydrogenation; saturated acids given 2.0 times the weight of iso-oleic acids. (Symbols for the different samples are the same as in Figure 25.)
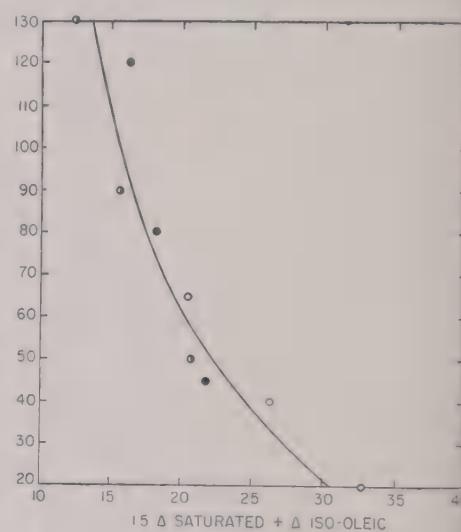
Fig. 27. Consistency of hydrogenated cottonseed oil at 22.5°C. in relation to amount of saturated and iso-oleic acids formed during hydrogenation; saturated acids given 1.5 times the weight of iso-oleic acids. (Symbols for samples are the same as Figures 25 and 26.)

the composite figure weighted about 1.5 to 1 in favor of the saturated acids formed, as in Figure 27. Obviously, the 1.5 to 1 rule is but a very rough approximation; since curves of slightly different slope are obtained for hydrogenation runs made under different conditions, the relationship will tend to vary, not only according to the operating conditions, but also according to the iodine value of the hydrogenated oil. In commercial practice, hydrogenation is not usually carried out under very nonselective conditions; hence a better correlation is usually obtained with the 2 to 1 weighting than with the weighting of 1.5 to 1.

The above laboratory results were from runs made under different conditions of temperature, pressure, agitation, and catalyst concentration.

ut with a single lot of catalyst. Somewhat different relationships may
e observed with different catalysts, *i.e.*, one catalyst may not only produce
  higher saturated acid content at a given iso-oleic acid content than
nother (and *vice versa*), but it may also tend to produce a firmer product
t a specific value of the composite 1.5 to 1 or 2.0 to 1 ratio of saturated
cids to iso-oleic acids figure. Comparative data for the laboratory hydro-
enation of cottonseed oil (under a number of different sets of conditions)
ith two different catalysts are shown in Figure 28.
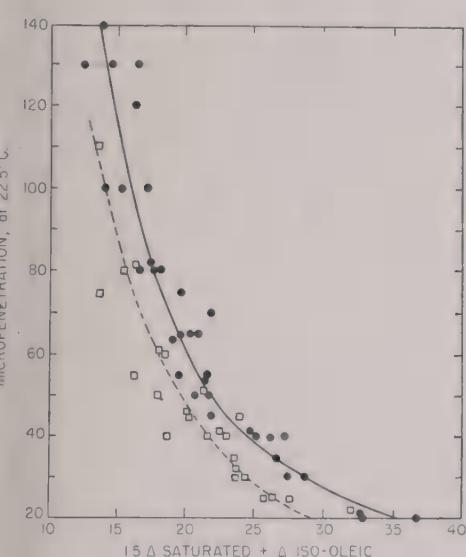
Fig. 28. Consistency of hydrogenated
cottonseed oil at 22.5°C. in relation to
amount of saturated and iso-oleic acids
formed during hydrogenation: compara-
tive results under widely varying condi-
tions with two different catalysts. (Circles
represent samples obtained with Catalyst
x; squares represent samples obtained
with Catalyst y.)
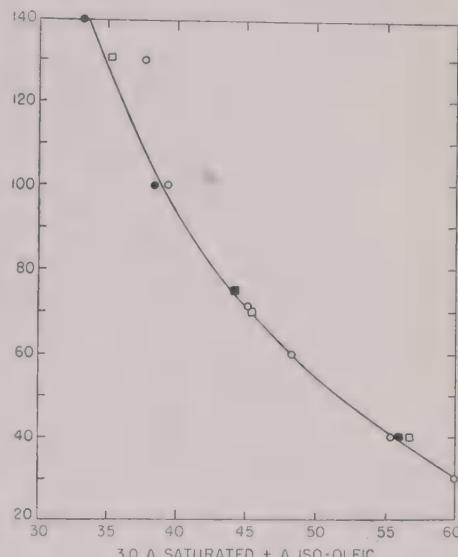
Fig. 29. Consistency of hydrogen-
ated soybean oil at 22.5°C. in relation
to amount of saturated and iso-oleic
acids formed during hydrogenation.
(Open circles and squares represent
samples obtained by moderately selec-
tive hydrogenation; closed circles and
squares represent samples obtained by
nonselective hydrogenation—see Table
71.)

  For the hydrogenated soybean oil samples, the least scattering of points
ccurs when the micropentrations at 22.5°C. are plotted against a compos-
e figure in which the amount of saturated acids formed is weighted
gainst the amount of iso-oleic acids formed in the ratio of 3.0 to 1
Fig. 29).
  As an indication of the relative effects of saturated acids and iso-oleic
cids in an oil originally even more unsaturated that soybean oil, reference
ay be made to the work of Fisher *et al.*[56] on hydrogenated linseed oils.

[56] G. S. Fisher, W. G. Bickford, and F. G. Dollear, *J. Am. Oil Chem. Soc., 24,*
79–382 (1947); G. S. Fisher, R. T. O'Connor, and F. G. Dollear, *ibid., 24,* 382–387
1947).

The results, with consistency expressed in terms of congeal point, rather than micropenetrations, as in the previous examples, are shown graphically in Figure 30. The best correlation, with selectively and nonselectively hydrogenated samples, is obtained when equal weight is given to the saturated and to the iso-oleic acids formed. Results of the same investigators on selectively and nonselectively hydrogenated cottonseed oils are also shown in the figure. It will be seen that for this oil the 2.0 to 1 weighting is valid for the congeal point as well as for the micropenetration relationship.
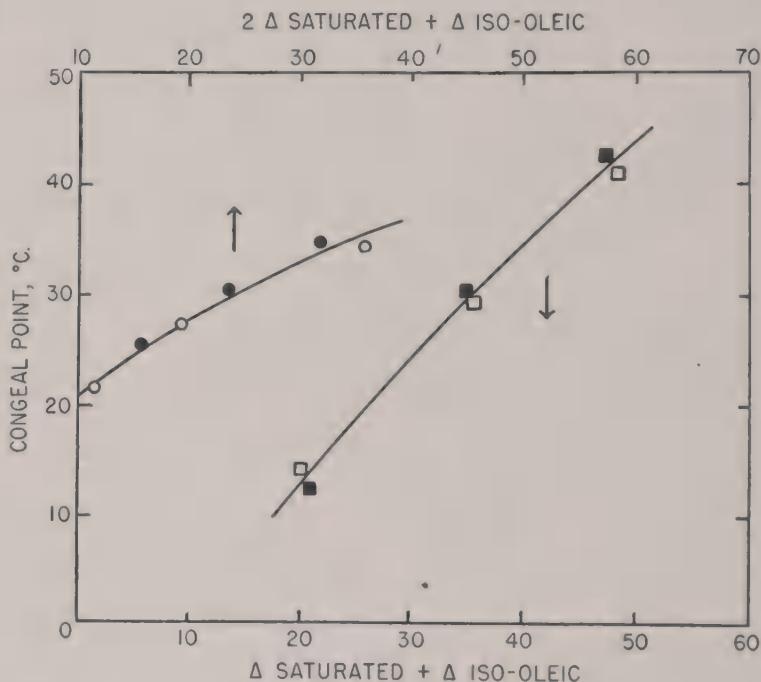
Fig. 30.   Consistency (as indicated by congeal point) of hydrogenated cottonseed and linseed oils in relation to amount of saturated and iso-oleic acids formed during hydrogenation. (Open circles represent samples of cottonseed oil selectively hydrogenated; closed circles represent cottonseed oil nonselectively hydrogenated; open squares represent linseed oil selectively hydrogenated; closed squares represent linseed oil nonselectively hydrogenated.)

The effect of different hydrogenation conditions on the 70–75°F. body of hydrogenated cottonseed oil may be judged from the data in Table 70, representing analytical values interpolated to a common iodine value of 63.6. It will be seen that at a given iodine value the fat is softest, i.e., the value [1.5 saturated acids formed + iso-oleic acids formed] is at a minimum and the micropenetration at 22.5°C. is at a maximum, when the conditions of hydrogenation are such as to produce only moderate selectivity. A harder product is obtained either by very selective hydrogenation

nonselective hydrogenation. The tests with soybean oil recorded in
able 71 do not show a similar effect, but only because none of the runs
ere made under extremely selective conditions. The first and third runs
this series show the adverse effects, referred to in Chapter XVII, of
drogenating with a relatively low concentration of nickel.

In view of the relatively low melting points of elaidic and other *trans-*
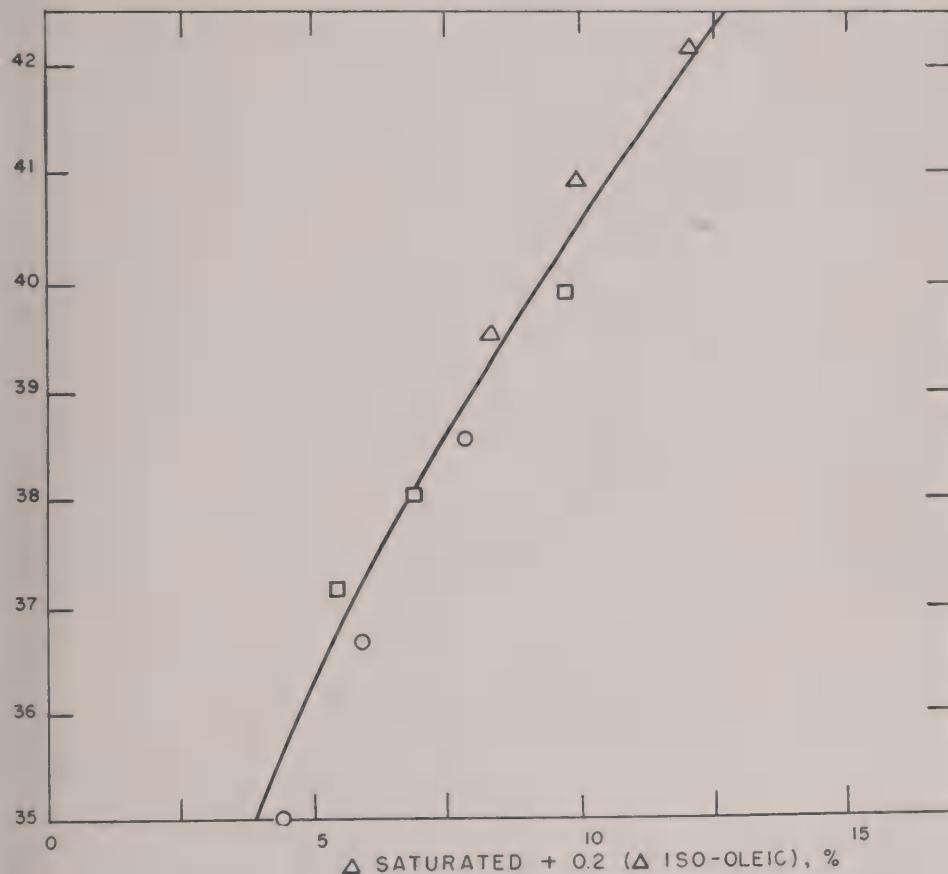
Fig. 31. Melting point of hydrogenated cottonseed oil in relationship to amount
saturated and iso-oleic acids formed during hydrogenation; saturated acids given
) times the weight of iso-oleic acids. Squares represent samples hydrogenated very
lectively; circles, samples hydrogenated with moderate selectivity; triangles,
mples hydrogenated nonselectively.[56a]

onoethenoid acids (*ca.* 25°C. below the melting point of stearic acid) it
not surprising that iso-oleic acids contribute relatively little to the high-
mperature body or to the melting point of hydrogenated fats. Actually.
cottonseed oil hydrogenated with varying degrees of selectivity to pro-
uce widely varying increments of iso-oleic and stearic acids, the best
orrelation between melting point and solid acids formed is obtained when

the latter are weighted in favor of the saturated acids in the ratio of about 5 to 1 (Fig. 31).[56a]

When mixtures of cottonseed and soybean oil are hydrogenated, the composition and characteristics of the product are intermediate between those of the unmixed oils hydrogenated under the same conditions. Certain representative analytical data on cottonseed oil, soybean oil, and a 50–50 mixture of the two are given in Table 72.

For information on methods of hydrogenation to produce different shortening stocks, reference should be made to Chapter XVII.

TABLE 72

COMPOSITION AND CHARACTERISTICS OF COTTONSEED OIL, SOYBEAN OIL, AND 50-50 MIXTURE HARDENED UNDER SAME CONDITIONS[a]

Oil	Iodine value	Micropen. at 22.5°C.	Fatty acids, %	
			Saturated	Iso-oleic
100% Cotton............	109.1	Unhardened oil	24.0	1.0
	71.1	90	31.6	6.7
	65.4	60	33.8	7.6
	59.6	40	36.3	7.7
50% cotton, 50% soybean..	117.5	Unhardened oil	19.8	1.6
	75.0	110	27.7	7.5
	69.8	75	28.9	7.9
	63.0	50	32.8	7.9
	58.8	40	35.7	9.8
100% soybean............	133.2	Unhardened oil	13.4	2.4
	84.0	140	22.2	9.1
	80.1	100	23.6	10.3
	74.7	70	25.6	11.1
	68.1	40	29.0	10.9
	62.6	30	33.1	10.9

[a] Hydrogenation conditions: 275°F., 60 p.s.i.g. pressure, high agitation. 0.05% nickel, 15-lb. batch in laboratory dead-end convertor.

(c) Stability of Hydrogenated Fats

It has been noted previously (chapter II) that the ability of a fat to withstand oxidation is not a function of its over-all degree of unsaturation, but rather is determined predominantly by its content of polyethenoid acids, or more accurately, by its concentration of active methylene groups, one such group being contributed by each normal linoleic acid radical and two being contributed by each linolenic acid radical. In accelerated stability tests such as the A.O.M. test, the rate of oxidation is inversely proportional to the keeping time. Therefore, if a series of samples is prepared by hydrogenating the same oil to different degrees, and the concentration of active methylene groups in each sample is plotted against the

[56a] A. E. Bailey, *J. Am. Oil Chem. Soc.*, *26*, 596–601 (1949).

reciprocal of the keeping time, an approximately straight line should
result. In practice, linear plots are, in fact, obtained. In Figure 32 are
representative plots from the data of Thompson[56b] on hydrogenated cot-
tonseed oil, and of Fisher and co-workers[56] on hydrogenated cottonseed
and peanut oils, and also hydrogenated linseed oil containing linolenic
acid.
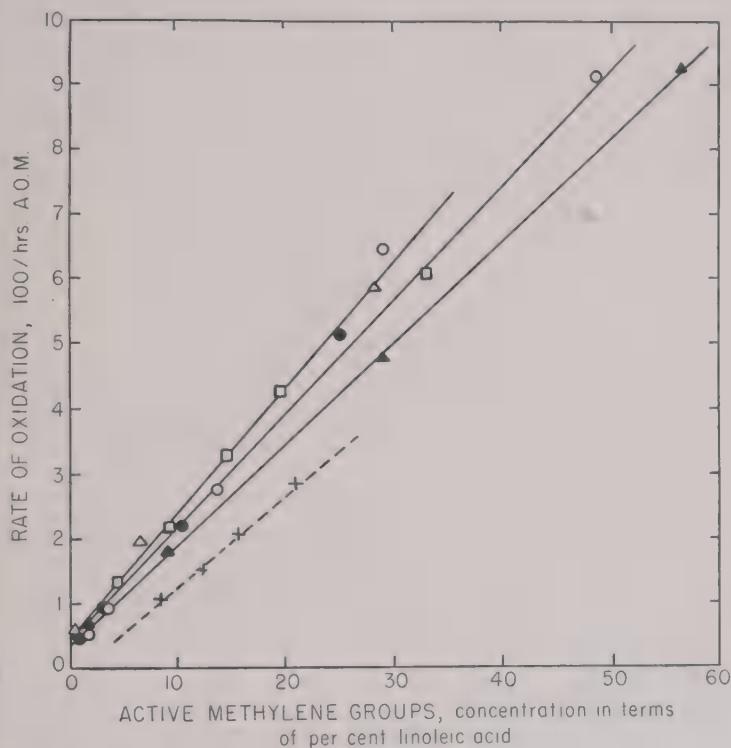
Fig. 32. Rate of oxidation of hydrogenated vegetable oils (reciprocal of stability)
as a function of their content of active methylene groups. (Different series of samples
are represented by symbols as follows: open circles, selectively hydrogenated cotton-
seed oil[56]; closed circles, nonselectively hydrogenated cottonseed oil[56]; open triangles,
selectively hydrogenated linseed oil[56]; closed triangles, nonselectively hydrogenated
linseed oil[56]; squares, selectively hydrogenated peanut oil[56]; crosses, hydrogenated
cottonseed oil.[56b]

Since most common oils do not differ significantly with respect to the
protective power of their natural antioxidants, the inherent stability of a
hydrogenated oil is largely a matter of how low the original oil may be
reduced in active methylene groups while the consistency is being reduced
to an acceptable value. Under equivalent conditions of hydrogenation,
different kinds of oil have considerably different capabilities in this

[56b] S. W. Thompson, Proceedings of the Committee on Food Research, Confer-
ence on Deterioration of Fats and Oils, Quartermaster Corps Manual 17-7 (1945).

respect. The data shown graphically in Figure 33 illustrate differences among four common oils. One of the oils, linseed, is not ordinarily considered an edible oil, but is included to show the effect of a very high initial proportion of linolenic acid. For the relationship of the iodine value to the active methylene groups in this figure the values of Fisher et al.[56] for moderately selective hydrogenation have been used. Inasmuch as these workers provided no information on the congeal points of their hydrogenated soybean oil samples, the arrow indicating a congeal point of
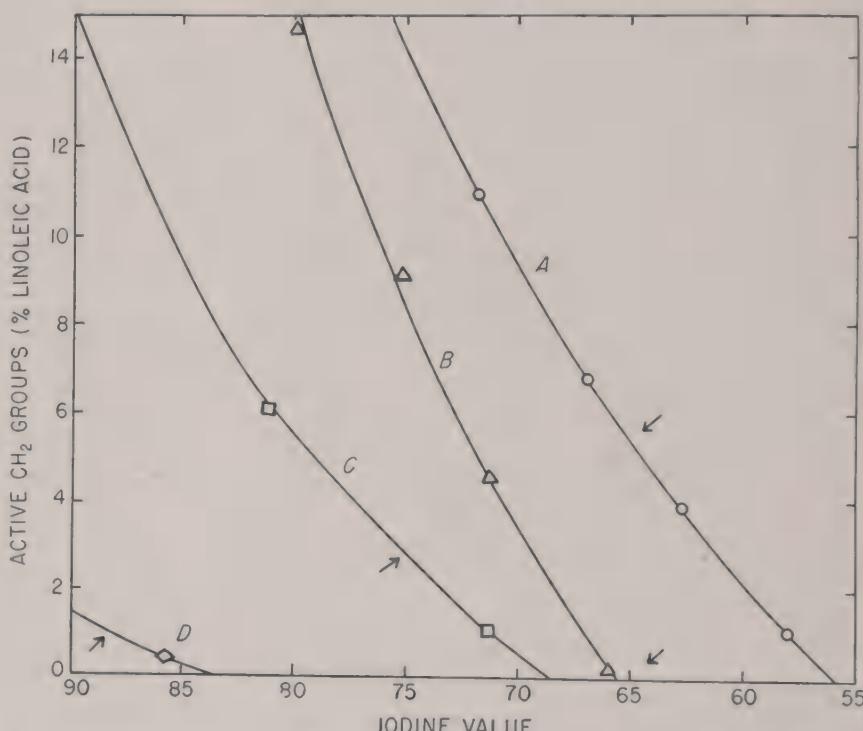
Fig. 33. Concentration of active methylene groups (in terms of percentage of linoleic acid) vs. iodine value for four different oils hydrogenated under moderately selective conditions: (A) cottonseed oil, (B) peanut oil, (C) soybean oil, (D) linseed oil. (Congeal point of 27.0°C. is indicated on each curve by the arrow.)

27.0°C. (a common value for shortening and margarine stocks) has been placed according to the data of Harrington et al.,[57] which appear to be representative of hydrogenation with more or less equal selectivity.

With respect to stability at equivalent consistencies (congeal points), the four oils stand in the order: peanut, linseed, soybean, cottonseed. This order is determined, of course, by the fatty acid composition of the raw oil. Peanut oil is very stable when hydrogenated, simply because its

[57] B. S. Harrington, F. B. Crist, A. A. Kiess, and W. A. Jacob, Oil & Soap, 22, 29–30 (1945).

riginal low concentration of linoleic acid permits this acid to be almost
ntirely eliminated before the product becomes very hard. Hydrogenated
ottonseed oil is the least stable because of its original high concentration
f saturated acids and its high ratio of linoleic to oleic acid. Hydrogenated
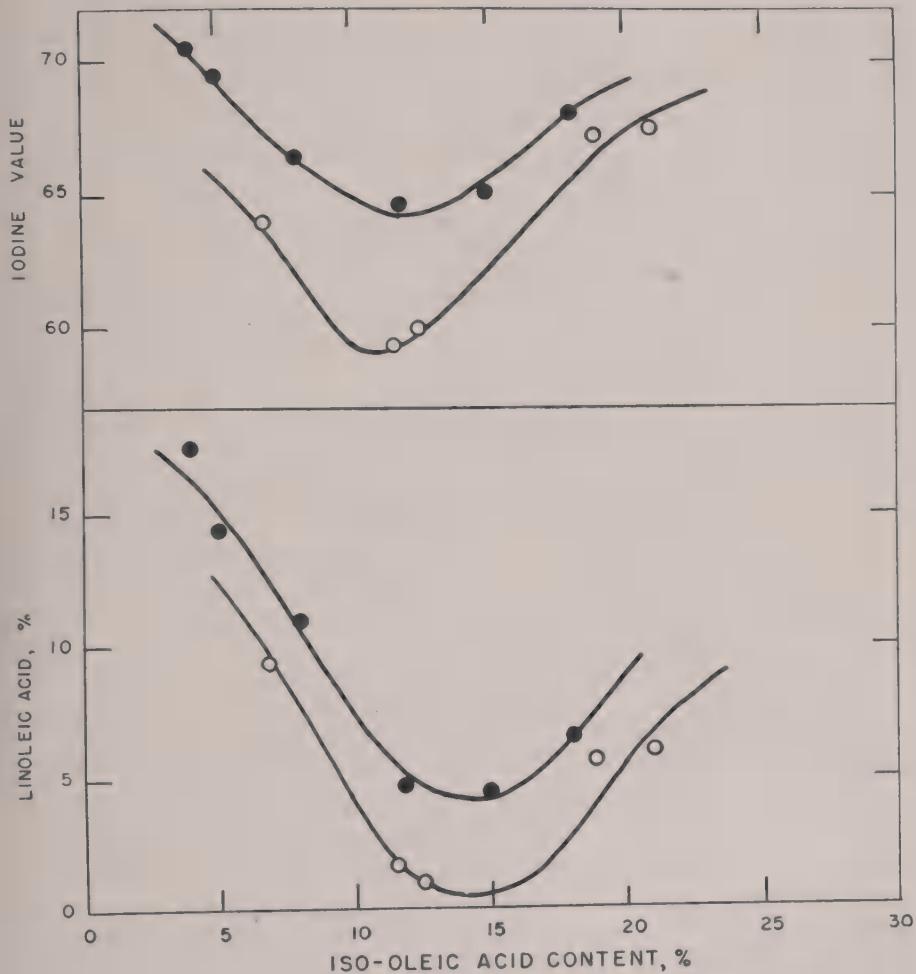
Fig. 34. Curves showing relationship between iodine value and linoleic acid
content, and amount of iso-oleic acids formed, in hydrogenating cottonseed oil to
shortening consistency (micropenetration of 65 at 22.5°C.) with varying degrees of
selectivity. Open circles and closed circles represent runs made with two different
catalysts.[56a]

linseed oil reaches the specified consistency at an iodine value much
higher than that of hydrogenated cottonseed oil, but the content of active
methylene groups is lower because the residual linoleic acid is so largely
in the isomeric 9:10, 15:16 form (see page 705). Soybean oil is likewise
higher in iodine value than cottonseed oil at the critical consistency, but

its content of active methylene groups is lower, partly because the percentage of saturated acids is lower initially, and partly because the octadecadienoic acids of the hydrogenated oil like those of hydrogenated linseed oil, consist in substantial part of the 9:10, 15:16 isomer.

In any single oil, the maximum stability (almost, but not quite, equivalent to the minimum iodine value) at shortening consistency is obtained when the oil is hydrogenated with only moderately high selectivity. If the selectivity is very high, the large amount of iso-oleic acids formed will limit the length to which hydrogenation may be carried. In cottonseed oil the optimum iso-oleic acids content for maximum stability is *ca.* 15% (Fig. 34).[56a]

Since vegetable oils naturally contain adequate amounts of tocopherols, a species of phenolic antioxidant, additional antioxidants of this type improve the stability relatively little, and are seldom, if ever, added. However, an acid-type synergist, usually commercial lecithin or phosphoric acid, is sometimes used to reinforce the action of the tocopherols. These two substances may be advantageously used in amounts up to about 0.02% and 0.004%, respectively, being preferably added before the shortening is deodorized.[57a] Since their effect is largely or entirely lost when the shortening is incorporated into baked goods, the practical advantage of their use is by no means as great as is indicated by accelerated oxidation tests on the pure fat.

(d) General Purpose Shortenings

The hydrogenation and blending of fats to produce so-called general purpose shortenings is described elsewhere (see pages 242–243 and 756–758. These shortenings are sold in large quantities for general bakeshop, restaurant, and hotel use, and also, with or without slight modification to increase the plastic range, are packed in sealed one- and three-pound tins for household use. In their manufacture a compromise is sought between a low iodine value, with high stability, and an extended range of plasticity. In general, the congeal point will range between 32.5 and 33.5°C. and the Wiley melting point between about 41 and 43°C. The minimum attainable iodine value will vary according to the composition; it may be as low as about 65 if the product consists largely or entirely of cottonseed oil, or as high as 70–75 if it contains much soybean oil. A low free fatty acid content (0.01–0.03%) and a correspondingly high smoke point is an invariable characteristic of good shortenings in this class. The color is practically never over 20 yellow and 2.0 red units (Lovibond-N″ scale), and in some brands is usually 1.0 red unit or less. The keeping quality, by the Swift or A.O.M. method is usually 70–90 hours.

[57a] A. E. Bailey and R. O. Feuge, *Oil & Soap, 21,* 286–288 (1944).

A large part of the all-hydrogenated shortening manufactured is con-
sumed by large commercial bakers and other users who are inclined to be
highly critical of the product. Obviously, for such a trade, it is necessary
to produce a shortening of as even quality as is possible. The manufac-
turers of the better brands of all-hydrogenated shortenings achieve a re-
markable degree of uniformity in their products; different batches of their
shortenings vary but little in appearance, texture, consistency, stability,
or behavior in baking operations. Various considerations involved in the
maintenance of shortening quality have been reviewed by Crapple.[57b]

(e) High-Stability Type Shortenings

The manufacture of crackers and sweet biscuits, to be sold in consum-
er's packages, presents a particular problem in stability, since long periods
of shipment and storage must at times intervene between the manufacture
of the article and its final consumption.

Products of this type are generally baked in large establishments, which
have facilities for conditioning their raw materials and conducting their
dough mixing operations at any desired temperature. When shortenings
are handled and used under such conditions it is not necessary for them to
be workable over any great range of temperature. Most manufacturers
of all-hydrogenated shortenings accordingly make a special product for
biscuits and crackers in which the plastic range of the fat is sacrificed
in favor of extremely high stability.

Biscuit and cracker-type shortenings which are made from cottonseed
oil usually have their linoleic acid content reduced to 3 or 4% or less,
and have a keeping time by the Swift method of 150 to 200 hours. An
iodine value of 60–64 and a congeal point of about 30–31°C. is usual. They
are relatively hard and brittle at temperatures below about 65°F., and
users, in addition to biscuit and cracker makers. Soybean oil is usually
are indistinguishable from ordinary all-hydrogenated shortenings. Short-
enings of this type are favored by some deep-fat food fryers and other
users, in addition to biscuit and cracker makers. Soybean oil is usually
omitted or held to a low percentage in the formula, because of the very
poor flavor stability of hydrogenated soybean oil which has been heated
to a high temperature.

(f) Superglycerinated Shortenings

Since about 1933, a special type of all-hydrogenated shortening with
superior emulsifying properties has been on the market. These shortenings
contain a greater proportion of combined glycerol than ordinary fats, in
the form of mono- and diglycerides. Mono- and diglycerides possess

[57b] G. A. Crapple, *J. Am. Oil Chem. Soc.*, *26*, 628–632 (1949).

marked surface activity, due to their content of both lipophilic (fatty acid) and hydrophilic (hydroxyl) groups, and are extremely effective in promoting dispersion of the shortening in baker's doughs, particularly those with a high content of sugar. The superior strength conferred upon the dough by the fine dispersion of the fat enables the baker to use a higher ratio of sugar to flour and other ingredients than with ordinary shortening. This circumstance has led to the use of the term "high-ratio" as applied to these shortenings.[58]   They are also described as "superglycerinated."

Superglycerinated shortenings have become extremely popular for use in cakes, sweet yeast doughs and similar products. A substantial part of the all-hydrogenated shortening used by commercial bakers is of this type and recently most of the leading manufacturers have adopted the practice of superglycerinating their all-hydrogenated shortening put up in household packages.

In appearance, taste, stability, etc., superglycerinated shortenings are not different from ordinary all-hydrogenated shortenings. Their content of free fatty acids is usually slightly high, amounting in various brands from 0.05 to 0.20%. The presence of free acids is claimed to be advantageous in a shortening used for cake making,[59] a slight increment of free acids naturally results from the method employed in making the mono- and diglycerides, and in some cases additional acids are apparently added.

Superglycerinated shortenings are readily recognized by their high glycerol content, and their low interfacial tension, as measured against water. They are suitable for uses other than cake making, but are not generally used for such commercially because of their high price; they usually sell for at least one cent per pound more than other shortenings. They are unsuitable for commercial deep-fat frying, because of the tendency of the mono- and diglycerides to decompose at high temperatures, with the production of free glycerol, and consequent smoking.

Both the manufacture of superglycerinated shortenings and their use in cakes and similar baked goods are covered by patents.[60,61]   Related products prepared from polyhydric alcohols other than glycerol have also been patented, as well as sulfated glycerides.[62,63]   Recently, certain partial sorbitol esters[64] and their derivatives[65] have been found to be effective

[58] The term "high-ratio" is copyrighted by the Procter and Gamble Co.

[59] V. M. Votaw and H. S. Coith (to Procter and Gamble Co.), U. S. Pats. 2,061,121 and 2,061,122 (1936).

[60] H. S. Coith, A. S. Richardson, and V. M. Votaw (to Procter & Gamble Co.), U. S. Pats. 2,132,393-8 (1938).

[61] A. K. Epstein and B. R. Harris (to Procter & Gamble), U. S. Pat. 2,132,406 (1938).

[62] B. R. Harris, U. S. Pat. 2,022,766 (1935).

[63] B. R. Harris (to Procter & Gamble Co.), U. S. Pats. 2,132,416-17 and 2,132,687 (1938).

[64] K. R. Brown (to Atlas Powder Co.), U. S. Pats. 2,303,432 (1942); 2,322,820-822 (1943).

[65] N. F. Johnston (to R. T. Vanderbilt Co.), U. S. Pat. 2,422,486 (1947).

mulsifying agents for cooking fats. These, however, have so far not been
ncorporated in manufactured shortenings, but are marketed separately
s addition agents. By reacting the simple sorbitol esters to different de-
rees with ethylene oxide, a series of products may be made with proper-
ies ranging from negligible water solubility (like the mono- and digly-
erides) to considerable water solubility. It is claimed that better baking
esults are obtained with a mixture which includes components which are
artially water-soluble.[65]   Commercial lecithin has often been recom-
ended as an emulsifying agent for baking fats, but its useful effect is
omparatively limited.

Superglycerinated shortenings are prepared simply by making up a
hortening stock in the usual way, and then, in the process of deodoriza-
on, adding about 6–8% of a commercial mono- and diglyceride prepa-
ation just before the end of the deodorization period.

If one of the new high-purity molecularly distilled monoglyceride prod-
cts is used, considerably less is required.[65a]

5. DRY SHORTENINGS

So-called "dry shortenings" are made by blending a plastic shortening,
sually of the all-hydrogenated type, in an emulsion with skim milk, and
pray-drying the mixture to form a powder containing 75–80% fat.[66]   The
omposition may also contain corn sugar or other carbohydrates,[67] and
ecithin, partial esters of glycerol or sorbitol,[68] or other emusifying agents.
Dry shortenings are used to some extent in preparing dry "ready-mixed"
roducts of low fat content, which require only the addition of water to
rm a batter ready for cooking. However, these products are more com-
only made with more or less conventional shortenings.

6. PEANUT BUTTER ADDITIVE

In recent years there has been considerable use of a preparation con-
sting of a large proportion of highly hydrogenated peanut oil particles
d salt, suspended in liquid peanut oil, as an additive for peanut butter
prevent oil separation. According to the patents covering the manufac-
re of this material,[69] it is essential for the hydrogenated oil to be sub-
antially in the β-phase if the suspension is to remain plastic and flow-
le, and not set up into a hard mass.

[65a] N. H. Kuhrt and E. A. Welch, J. Am .Oil Chem. Soc., 27, 344–346 (1950).
[66] E. J. Fechner (to Page Milk Co.), U. S. Pat. 2.065,675 (1936).
[67] G. H. Kraft (to Kraft-Phoenix Cheese Corp.), U. S. Pat. 2,035,899 (1936).
[68] G. C. North. A. J. Alton, and L. Little (to Beatrice Creamery Co.), U. S. Pats.
31.497–498 (1947).
[69] P. J. Mitchell, Jr. (to Procter and Gamble Co.), U. S. Pat. 2,521, 242 (1950).
W. Holman and O. T. Quimby (to Procter and Gamble Co.), U. S. Pat. 2,521,219
950).

BUTTER AND MARGARINE

A. Introduction

Despite the present upward trend in the production and consumption of vegetable oils, butterfat continues to be by far the most important individual oil or fat. The normal world production of butter has been reliably estimated to be as high as 4,000,000 metric tons, or 8,800,000,000 pounds annually.[1] Thus the production of butterfat is probably twice that of any other two oils or fats combined. In point of value, butterfat occupies an even more dominant position, inasmuch as it generally sells at a price much above that of ordinary edible fats.

Most of the butter produced is derived from cow's milk, although there are certain sections of the world where appreciable quantities are made from the milk of other animals. In India, for example, the production of buffalo butterfat or ghee is considerable. The present discussion will be confined to ordinary cow's butter, particularly as it is manufactured in the United States.

The manufacture of margarine or butter substitutes is a very large industry. In the United States the consumption of margarine has, until recently, never approached that of other edible fat products, owing to the plentiful supply of butter, and the custom of consuming much fat in the form of lard or shortenings. Even now the consumption is much lower than that of butter (5.7 pounds per capita in 1949). In Europe the use of margarine is much more widespread, because of the relative scarcity of butter and lard, and the custom of using margarine rather than shortening for general cooking purposes. In Great Britain, Germany, and the Low Countries, the yearly per capita consumption has in the past varied from 10 to 20 pounds per year. In Norway it has averaged more than 30 pounds, and in Denmark it has been as high as 45 pounds.[1a]

Data on the production and consumption of butter and margarine in the United States in recent years are given in Table 73. Since World War II, butter production has markedly decreased, owing to a large demand

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[1] International Institute of Agriculture, *Oils and Fats: Production and International Trade*, Rome, 1939.

[1a] K. Snodgrass, *Margarine as a Butter Substitute*. Food Research Institute, Stanford University, 1930.

nd high prices for fluid milk in relation to other dairy products; and the
onsumption of margarine has increased, although not in proportion to the
lecrease in butter consumption.

Since the repeal of the Federal tax on uncolored margarine early in
.950, the ratio of colored to uncolored margarine has increased greatly.
[n October 1950 production of uncolored margarine was 23,808,000
)ounds, and of colored margarine 50,132,000 pounds.

TABLE 73

PRODUCTION (MILLIONS OF POUNDS) OF BUTTER AND MARGARINE IN UNITED STATES[a]

	Margarine				Butter			
Year	Colored	Un-colored	Total	Civilian consump-tion	At cream-eries	On farms	Total	Civilian consump-tion
1915	7.7	134.3	142.0	138.8	780	971	1751	1728
1919	19.2	349.6	368.8	353.9	939	708	1646	1602
1925	12.2	221.8	234.0	232.0	1456	619	2074	2054
1939	1.4	299.4	300.9	300.9	1782	429	2210	2276
1942	64.5	361.3	425.7	364.0	1764	366	2130	2093
1943	116.5	497.6	614.1	501.0	1674	341	2015	1525
1944	107.6	480.6	588.2	497.0	1489	329	1818	1534
1945	98.9	515.1	614.0	525.0	1364	337	1701	1415
1946	58.1	514.5	572.5	533.0	1171	334	1505	1459
1947	59.1	686.9	745.9	713.9	1330	316	1646	1605
1948	96.4	812.3	908.7	891.0	1214	299	1513	1459

[a] Bureau of Agricultural Economics, U. S. Dept. Agr., *The Fats and Oils Situation*,
June, 1949.

TABLE 74

AVERAGE WHOLESALE PRICES (CENTS PER POUND) OF BUTTER, MARGARINE, AND CRUDE
COTTONSEED OIL IN UNITED STATES DURING SPECIFIED PERIODS[a]

	Av., 1935–1939	1941	1943	1946	1947	Nov., 1950
Butter, 92-score, Chicago......	29.3	34.3	44.0	61.9	70.6	64.0
Margarine, vegetable 1-lb. car-tons, Chicago...............	15.3	15.8	19.0	23.0	36.9	29.8
Crude cottonseed oil, tank cars, mills.....................	7.6	9.5	12.8	15.8	25.9	20.6

[a] U. S. Dept. Agr., *Agricultural Statistics*, 1946 and 1949. Bureau of Agricultural
Economics, U. S. Dept. Agr., *The Fats and Oils Situation*, December, 1950.

The principal butter-producing states are, in order: Minnesota, Iowa,
nd Wisconsin. Following the United States, the countries normally pro-
ucing the greatest amounts of butter are, in order: Germany, France,
.ustralia, Denmark, New Zealand, Canada, and the Netherlands. Den-
1ark, New Zealand, Australia, and the Netherlands all have a large ex-
ortable surplus of butter.

Average wholesale prices of butter and margarine on the United States market in recent years are shown in Table 74. For comparison with the price of margarine, the same table also shows corresponding prices of crude cottonseed oil, which is the chief raw material for margarine manufacture in this country.

Before proceeding to a further discussion of butter and margarine, an important difference is to be noted in the technology of these two products. Since the fat used in making margarine is a manufactured product, it is subject to wide variations in quality and characteristics. Although the nonfatty constituents are certainly of concern to the margarine manufacturer, they are usually of minor interest, in comparison with the fat. On the other hand, butterfat is a natural product, which is not commonly modified by processing treatment. Consequently, the technology of butter is concerned with substances other than fat, and is in fact, largely the province of the bacteriologist rather than the oil and fat chemist. No attempt will be made here to cover the bacteriology of butter in other than a very cursory manner.

B. Butter[2]

1. Varieties and Grades

The definitions which are recognized by the United States Department of Agriculture for butter and materials from which butter are derived are as follows:

Butter. The food product usually known as butter, and which is made exclusively from milk or cream, or both, with or without common salt, and with or without additional coloring matter. It contains not less than 80 percent by weight of milk fat, all tolerances having been allowed for.

Cream. That portion of milk, rich in milk fat, which rises to the surface of milk on standing or is separated from it by centrifugal force.

Milk. The whole, fresh lacteal secretion obtained by the complete milking of one or more healthy cows, excluding that obtained within 15 days before and 5 days after calving, or such longer period as may be necessary to render the milk practically colostrum-free. The name "milk" unqualified means cow's milk.

Butter may be produced from either sweet or ripened cream, and may be either salted or unsalted. The butter produced in factories in the United States is distinguished from that produced on farms by the designation "creamery butter." The production of both sweet cream and unsalted butter in this country is limited; by far the greatest part of the creamery butter is made from ripened cream and is salted.

The production of creamery butter now greatly exceeds that of farm butter in the United States, amounting in recent years to about 80% of

[2] General References: O. F. Hunziker. *The Butter Industry,* 3rd ed., published by the author, La Grange, Illinois, 1940. G. H. Wilster, *Practical Butter Manufacture,* 5th ed., Oregon State College Cooperative Association, Corvallis, Oregon, 1946.

the total. There are several points of difference in the manufacture of farm and creamery butter, each of which contributes to distinctive properties in the product. On the farm, the cream is generally permitted to ripen spontaneously, through the action of whatever microorganisms that happen to be naturally present. The common practice in creameries is to destroy the bulk of the natural organisms in the cream through pasteurization, and conduct the ripening through the agency of special bacterial cultures, which are chosen for their ability to produce the most pleasing aroma and flavor in the butter. Consequently, the flavor of creamery butter is more uniform and is inclined to be somewhat stronger than that of farm butter. The consistency of creamery butter is also somewhat more uniform, due to the fact that it represents the average characteristics of the fat from a larger number of different cows. Creamery butter is commonly colored artificially to a consistent yellow hue; butter made on the farm is usually not colored, and it consequently varies considerably in depth of yellow color, with the season of the year and the feed of the dairy herds.

The grade of creamery butter is assigned on the basis of a score which depends upon its flavor and aroma and its physical characteristics, as determined by inspection. Scores range from 100 downward, although actually a score higher than 93 is seldom awarded, and most butter on the market is in the range 90 to 93, inclusive. According to standards made effective by the U. S. Department of Agriculture on February 1, 1943, official U. S. grades correspond to the following scores:

Grade AA.............93 score
Grade A..............92 score
Grade B..............90 score
Grade C..............89 score
Cooking grade......... —
No grade.............. —

A minor amount of creamery butter is produced from the butterfat remaining in the whey resulting from the manufacture of cheese. The annual production of whey butter in the United States before World War II amounted to about 25,000,000 pounds. About 2,500,000 pounds of process or renovated butter was also produced, by separating and re-emulsifying, as in margarine manufacture, the fat of butter which was off in flavor or had deteriorated badly in storage. Most of the process butter produced is either exported or utilized by commercial bakeries.

2. STRUCTURE AND COMPOSITION

Butter consists of a matrix of plastic fat enclosing an aqueous phase of buttermilk and water, which is dispersed in the fat in the form of very small droplets. Any salt which may have been incorporated in the butter is dissolved in the aqueous phase. The buttermilk, of course, contains a characteristic proportion of casein, minerals, and other soluble milk solids.

Butter usually contains about 0.2% of phosphatides, calculated as lecithin. A small amount of air is incorporated in the fat during the operations of kneading and working. The content of air by volume usually amounts to 1 to 5%.

Butter is commonly spoken of as an emulsion. However, the fact that the fatty phase is a plastic solid rather than a liquid gives the product distinctive physical characteristics. The plasticity of butter is sufficient to prevent separation of the two phases at ordinary temperatures, even though highly effective emulsifying agents are present, in the form of proteins, phosphatides, etc. When the fat is heated, as in the frying of foods, these emulsifying agents prevent the coalescence of water droplets and permit the water to escape quietly, with foaming of the fat, rather than spurting or spattering.

The fat content of creamery butter varies according to the legal requirements in this particular in the various countries in which it is sold. In the United States the fat content is usually between 80 and 81%. In certain European countries it is a little higher. The salt content of butter in the United States ranges between about 1.5 and 3.0%; the butter marketed in Europe usually contains somewhat less salt, e.g., about 1%. The average content of casein (curd) and other milk solids is about 1.0%. The remainder of the product is, of course, water.

Butter is an important source of vitamin A, and to a lesser extent, of vitamin D. The vitamin content of butterfat, the component fatty acids and glycerides, etc., are discussed in Chapter VI.

3. FLAVOR AND AROMA

The source or sources of the distinctive flavor and aroma of butter have long been a matter for discussion and conjecture. Until quite recently butter flavor has been attributed primarily to the butyric acid present in the butterfat glycerides in combination with lactic acid resulting from the fermentation of milk sugar. It has also been suggested that the protein and phospholipid substances in the butter may contribute to its flavor. It is now definitely established, however, that the flavor and odor is principally derived from the compound diacetyl, $CH_3.CO.CO.CH_3$, which is formed by the bacterial fermentation of citrates in the milk. The bacteria used in the controlled ripening of cream for butter manufacture are mixed cultures of various species of *Streptococci*, especially chosen for their ability to ferment lactose and citrates, with the production of this and other flavor- and odor-giving substances.

The bacteriology of dairy butter, in relation to the development of flavor and aroma, has been extensively studied by Hammer and asso-

ciates,[3] who have fully elucidated the mechanism of diacetyl formation. It has been demonstrated that the first product of citrate fermentation is acetylmethylcarbinol, $CH_3.CO.CH(OH).CH_3$. This compound is relatively lacking in odor and flavor, but under the proper influences it may be oxidized to the more strongly flavored diacetyl. Atmospheric oxygen is necessary for the reaction, but as pointed out by Michaelian and Hammer,[4] the latter actually is the result of bacterial action rather than chemical oxidation.

Good butter cultures contain both acetylmethylcarbinol and diacetyl; they may be recognized by the creatine test[5] for the combined content of these two compounds. The ratio between these two compounds in the culture itself is not a matter of particular importance, as oxidation of acetylmethylcarbinol to diacetyl will largely occur in the processes of preparing the starter and ripening the cream. The ratio of acetylmethylcarbinol to diacetyl in the finished butter is said to commonly be about 15 to 1.

The following values are given by Shrader[6] for the diacetyl content of various butters: low-flavored butter, 0.1 to 0.3 p.p.m.; butter of medium flavor, 0.4 to 0.8 p.p.m.; full-flavored butter, 0.9 to 2.0 p.p.m. The species of *Streptococci* which are effective in the fermentation of citrates are in general distinct from those responsible for the formation of lactic acid. The cultures which are used commercially are mixtures of special strains of both types which have been carefully selected for their odor- and flavor-producing characteristics. Certain varieties of bacteria which may be present in milk and cream have the property of reducing acetylmethylcarbinol or diacetyl to 2,3-butylene glycol, $CH_3.CH(OH).CH(OH).CH_3$.[7] Such reduction is undesirable if it occurs to any considerable extent. Other compounds known to contribute to the flavor of butter include acetic and propionic acids produced from the lactose in the milk by bacterial action.[8]

In the preparation of margarines, the same cultures are used as in the manufacture of butter and the manufacturing process involves a similar series of reactions. Yet there is a subtle difference between the flavor of margarine and butter. This would seem to indicate that the content of

[3] B. W. Hammer, *Dairy Bacteriology*. 2nd ed., Wiley, New York, 1938. B. W. Hammer and F. J. Babel, *J. Dairy Sci.*, *26*, 83–168 (1943).

[4] M. B. Michaelian and B. W. Hammer, *Iowa State Coll. Agr. Mech. Arts, Agr. Expt. Sta., Research Bull.*, *205*, 203–214 (1936).

[5] B. W. Hammer, *J. Dairy Sci.*, *18*, 579–581 (1935).

[6] J. H. Shrader, *Food Control*. Wiley, New York, 1939.

[7] G. L. Stahly, B. W. Hammer, M. B. Michaelian, and C. H. Werkman, *Proc. Iowa Acad. Sci.*, *42*, 73–76 (1935).

[8] B. W. Hammer and F. F. Sherwood, *Iowa State Coll. Agr. Mech. Arts, Agr. Expt. Sta., Research Bull.*, No. 80 (1923).

buytric acid or other substances peculiar to butterfat may in some way influence the development of the true butter flavor.

4. Consistency and Texture

The iodine value and the consequent consistency of butterfat is considerably affected by the feed of the dairy herds. Since the feed necessarily varies somewhat from summer to winter, there are well-defined seasonal changes in the consistency of butter. Dean and Hilditch[9] have noted the tendency of unsaturated acids in the fat to increase and saturated acids to decrease as the animals are taken off winter feeds and put on summer pasturage. These authors have also noted an increase of unsaturation in the butterfat of individual cows, as their age increases.

The more detailed data on the effect of specific feedstuffs are from European rather than American sources, due to the greater variety of oilcakes and other concentrated feeds which are available for use in Europe. The reports of Hansen and Steensberg[10] and Hansson and Oloffson[11] indicate the effect of a variety of feeds. The former authors divide commercial samples of butter into three different classes, as follows: (a) very soft butter, with an iodine value over 35; (b) normal butter, with an iodine value of 29.4 to 35, and (c) hard, brittle or dry butter, with an iodine value below 29.4. The feeds which tended to produce the above classes of butter were broadly as follows: (a) sesame, sunflower, linseed, and rapeseed cakes, soybeans, and dried corn distillery mash; (b) peanut, cottonseed, and soybean cakes, potato distillery mash, barley, oats, and wheat bran; (c) coconut, palm kernel, and babassu cakes, peas, and other legumes low in oil content.

Of the various forms of pasturage, red clover was found to produce the softest butter,[11] with an iodine value in excess of 40. In the form of hay or ensilage, however, the softening effect of green materials was largely lost. Different cows on the same rations produced butterfat varying in iodine value by as much as 6 or 7 units. About 8 days of feeding on a specific ration was required to produce the characteristic effect of the feed. In general, the higher the iodine value of the oil in an oilcake, the softer was the butterfat. However, the effect of different oils may be more closely related to their content of saturated acids than to their over-all degree of unsaturation. In the United States it has been generally noted that the

[9] H. K. Dean and T. P. Hilditch, *Biochem. J.*, 27, 889–897 (1933).
[10] A. P. Hansen and V. Steenberg. *9th Beretning fra Statens Forsøysmejeri, 1931*, 95 pp.; *Landw. Rundschau*, 8, 201–202 (1931).
[11] N. Hansson and N. E. Olofsson, *Biedermanns Zentr. B. Tierernähr.*, 3, 352–391 (1931); *Kgl. Landtbruks-Akad. Handl. Tid.*, 70, 621–655 (1931).
[12] E. W. Neasham and A. J. Gelpi, *Natl. Butter Cheese J.*, 25, No. 1, 12–13 (1934); W. D. Gallup, *Ind. Eng. Chem., Anal. Ed.*, 8, 123–124 (1936).

feeding of cottonseed cake tends to produce hard butter.[12]   With other conditions the same, Jersey and Guernsey cows produce a butterfat lower in iodine value and firmer in consistency than do Ayrshires or Holsteins.[13]   Data on the consistency of typical samples of soft and firm butter will be found in Table 75.

It is well recognized that the firmness of butter is somewhat influenced by the treatment of the cream prior to churning. If the cream is not chilled to a sufficiently low temperature (ca. 40°F. or below), or is not held at this temperature for a sufficient time (at least 3–4 hours), the butter will tend to be too soft and melt too readily. This effect is presumably to be attributed to supercooling of the fat and failure to deposit fat crystals, although it is not clear why subsequent cold storage should not completely remedy the defect.

TABLE 75

MICROPENETRATIONS AND ESTIMATED SOLIDS CONTENTS[a] AT DIFFERENT TEMPERATURES OF FAT FROM TYPICAL SAMPLES OF BUTTER AND MARGARINE

| | Butter | | | | Margarine | | | |
| | Soft | | Firm | | European[b] | | American[c] | |
Temp., °C.	Micro-pen., mm./10[d]	Solids, %	Micro-pen., mm./10[d]	Solids, %	Micro-pen., mm./10[d]	Solids, %	Micro-pen., mm./10[d]	Solids, %
45	—	0	—	0	—	0	—	0
40	—	0	—	0	—	0	—	0.2
35	—	0.7	—	2.0	—	0	—	3.0
30	—	4.0	367	7.5	—	4.5	357	8.0
25	—	8.5	145	13.0	—	11.5	117	16.0
20	—	14.5	43	22.0	—	18.5	41	24.0
15	—	21.5	17	36.0	—	25.5	19	31.0

[a] Estimated dilatometrically.
[b] Of unknown composition.
[c] Margarine fat (Nucoa) prepared by selectively hydrogenating cottonseed oil and soybean oil.
[d] By the method of R. O. Feuge and A. E. Bailey, Oil & Soap, 21, 78–84 (1944).

The texture of butter, as distinguished from its consistency, is highly important, and the attainment of proper texture may be said to amount very nearly to an art. For the best texture it appears essential to preserve something of the original structure of the fat globules, as they exist in the cream. If the product is given such prolonged mechanical working (or churning) as to destroy this structure, and thereby assumes the perfectly smooth texture of lard or a shortening, it will become undesirably "greasy" or "salvy." On the other hand, some degree of working is essential for the incorporation of salt and the dispersion and uniform

[13] O. F. Hunziker, G. Spitzer, and H. C. Mills, Purdue Bulletin 159 (1912).

distribution of milk droplets, to prevent the product from being "leaky."
Overworking is also considered to contribute to "stickiness" in butter
made from a relatively firm butterfat.

5. Spoilage

Much of the spoilage occurring in butter is in a somewhat different
category from that which takes place in other edible fats. Whereas the
deterioration of lard, shortenings, and salad oils is almost wholly the re-
sult of atmospheric oxidation, bacterial and mold action may enter largely
into the deterioration of butter (and margarine).

One of the purposes of incorporating salt into butter is for its preserva-
tive action. The presence of 2–3 parts of salt per 15 parts of water in the
product is sufficient to inhibit the growth of microorganisms in the aque-
ous phase or at the water–fat interface. It is probable, however, that the
practice of incorporating salt in the separated butter does not result in an
even distribution of salt through the product, and that some of the very
small water droplets may escape contact with this preservative. Bacterial
action within such droplets, however, is highly localized.

A fairly common and very objectionable flavor defect in butter is the
appearance of "fishiness." The subject of fishy flavor has been investigated
by Davies and Gill,[14] who ascribe fishiness to trimethylamine derived
from phosphatides in the fat. For some reason as yet unknown, highly
unsaturated fatty acids in the fat are necessary for the development of
fishy flavor; hence this phenomenon may be classed with the flavor rever-
sion which occurs in soybean oil, linseed oil, etc., and which likewise is
often of a fishy character. There do not appear to be more than traces of
linolenic acid in butterfat,[15,16] but the presence of highly unsaturated C_{20}
and C_{22} acids has been reported.[15]

The development of fishiness appears to be promoted by the churning
of cream high in (lactic) acid, by the presence of salt, and by copper salts
or other metallic pro-oxidants.[17]

Deterioration of butter through oxidation is evidenced by a pronounced
"tallowy" flavor. This flavor appears with very slight oxidation of the fat;
in some cases it may become evident simultaneously with the first de-
tectable concentration of peroxides.[18] True oxidative rancidity in butter
is rarely encountered, partly because the over-all degree of unsaturation

[14] W. L. Davies and E. Gill, *J. Soc. Chem. Ind.*, *55*, 141–146T (1936).
[15] A. W. Bosworth and J. B. Brown, *J. Biol. Chem.*, *103*, 115–134 (1933). T. P.
Hilditch and H. Jasperson, *J. Soc. Chem. Ind.*, *60*, 305–310 (1941).
[16] H. C. Eckstein, *J. Biol. Chem.*, *103*, 135–140 (1933).
[17] See, for example, H. H. Sommer and B. J. Smit, *Wisconsin Agr. Expt. Sta.,
Research Bull.*, *57* (1923).
[18] V. C. Stebnitz and H. H. Sommer, *Oil & Soap*, *14*, 228–232 (1937).

in the fat is low, and partly because oxidation is very slow at the low temperatures at which butter is stored. At true cold storage temperatures, butter deteriorates very little and may be satisfactorily stored for months without significant loss of flavor or of vitamin A content.[19]

6. Butter Manufacture

(a) Treatment of Cream

The cream used for the manufacture of creamery butter is for the most part collected from farms, where it is separated from the milk by centrifugal separators. The fat content varies from about 30 to 40%, averaging perhaps 35%. Cream of relatively high fat content is preferred, as it gives a lower loss of butterfat in churning.

Upon arrival at the creamery sufficient natural fermentation has often occurred to increase the titratable acidity (calculated as lactic acid) to 0.4–0.6%. For easy churning and the best flavor and keeping quality in the butter this must be reduced to about 0.10–0.25%. So-called neutralization for this purpose is carried out by treating the fat with suitable alkaline substances; sodium bicarbonate is usually employed, although there is some use of sodium carbonate, alone or mixed with bicarbonate, and also of calcium and magnesium hydroxides. Following neutralization, the cream is pasteurized in the usual way; and carbon dioxide remaining from neutralization is removed during pasteurization, and often a spraying or stripping treatment under vacuum is combined with pasteurization, to remove weed flavors or other undesirable odors and flavors.

As mentioned previously, ripening of the neutralized and pasteurized cream is carried out with the assistance of special bacterial cultures. Inoculation of the cream is not carried out directly from the mother culture of bacteria, but is effected through the intermediate use of a "starter," prepared from the mother culture and relatively large batches of pasteurized milk.

For the preparation of starters either whole or skim milk may be employed. Slatter[20] recommends the use of whole milk, preferably from Jersey or Guernsey cows, because of the high content of citrates in the milk obtained from these breeds. The presence of citrates is essential because they are the precursors of the diacetyl which contributes largely to the flavor of butter. The addition of a few hundredths of one per cent of citric acid or sodium citrate is recommended by some authorities.[21,22]

[19] R. Jenness and L. S. Palmer, *J. Dairy Sci.*, 28, 473–494 (1945).
[20] W. L. Slatter, *Natl. Butter Cheese J.*, 28, No. 17, 38–39 (1937).
[21] M. B. Michaelian, R. S. Farmer, and B. W. Hammer, *Iowa State Coll. Agr. Mech. Arts, Agr. Expt. Sta., Research Bull.*, 155, 325–360 (1933).
[22] H. L. Templeton and H. H. Sommer, *J. Dairy Sci.*, 18, 97–104 (1935).

The fermentation of citrates is an aerobic process; Hammer[23] suggests aeration of the milk under pressure during preparation of the starter.

The amount of starter mixed with the cream is usually about 5%, although in some cases somewhat more may be used. The production of the substances which give butter its characteristic odor and flavor occurs partly in the starter and partly after the latter is added to the cream. Ripening is almost never carried out at a temperature in excess of 70°F., and it is often conducted at 50–55°F. At the lower temperatures an overnight period of ripening is sufficient; this may be reduced to a few hours at 65–70°F. It is, of course, desired that the flavor-promoting fermentations predominate over other fermentations produced by fortuitous bacterial action, and this is best insured by using a relatively low ripening temperature and a correspondingly long time.

The acidity of the cream should rise only slightly during controlled ripening, as lactic acid production comprises but a minor part of the process. Although adjustment of the acidity is commonly made only before pasteurization, it is, of course, the acidity of the butter serum that is important. According to Hunziker,[24] this should on no account exceed 0.477%. According to some writers, adjustment of the acidity is best done on the basis of the pH of the serum, rather than its titratable acidity. Golding[25] has recommended a pH of 6.1 to 6.8 in the milk serum of butter. In recent years there appears to have been a tendency to carry the acidity lower and lower, and some authorities now recommend a titratable acidity of about 0.10% or a pH of 6.6–7.0, or even higher. It is to be noted that, while higher acidities may produce butter grading slightly higher in flavor when it is processed, low-acid butter retains it flavor much better in storage.

(b) Churning and Subsequent Operations

After the cream is brought to the proper condition by bacterial action, it is churned in large rotary churns. The churning operation results in a breaking up of the fat-in-water type emulsion existing in the cream, with the resultant separation of the butterfat in the form of relatively large, coherent masses.

The physicochemical nature of the churning operation has been much debated by dairy technologists and does not yet appear to be satisfactorily explained in all particulars. The so-called foam theory of Rahn[26] has been in vogue for a considerable time. This theory accounts for the coalescence of fat globules during churning by postulating a denaturation through

[23] B. W. Hammer, *Dairy Bacteriology.* 2nd ed., Wiley, New York, 1938.
[24] See footnote 2.
[25] N. S. Golding, *Proc. Ann. State Coll. Wash. Inst. Dairying,* 6, 37–41 (1933).
[26] O. Rahn, *Forsch. Gebiete Milchw. Molkereiwes.,* 1, 309–325 (1921).

aeration of the surface-active materials which stabilize the globules. The more recent investigations of Palmer and Wiese[27,28] would indicate that coalescence takes place simply through a phase inversion of the emulsion, following removal of these materials from the surface of the globules by erosion, since the protein-phosphatide substances which are active at the fat–water interface are largely recovered in the buttermilk.

With a given lot of cream, the churning properties appear to be related to the plasticity of the butterfat; hence the cream must not only be brought to the proper temperature, but must also be held at that temperature long enough for a sufficient degree of fat crystallization to occur. During churning the fat globules must be sufficiently soft and plastic to coalesce readily, yet not soft enough for large aggregates of fat to appear while uncoalesced globules remain.

The temperatures recommended for churning range from about 48–52°F. in the spring and summer when the melting point of the butterfat is low and the viscosity of the cream is low, to about 53–60°F. in the fall and winter, when contrary conditions prevail. For cream containing very hard butterfat, as may be produced, for example, by feeding cottonseed meal, a churning temperature as high as 70°F. may be used. The temperature should be such that churning will require about 40–50 minutes. At excessively low temperatures churning will require an inordinate time; at high temperatures churning is quickly completed, but an excessive amount of fat will remain in the buttermilk, and the butter tends to be greasy in texture. Under favorable conditions the fat lost in the buttermilk averages less than 1% of the total amount in the cream. Cream with relatively large fat globules churns more readily than cream in which small globules predominate. For this reason, cream from Jerseys and Guernseys tends to churn more easily than cream from Holsteins and Ayreshires, and the difficulty of churning tends to increase as the period of lactation advances. Sweet cream churns more slowly than sour cream. Butter color is usually added to the cream just before churning is started.

The churns used in creameries almost invariably consist of large horizontal cylinders, usually made of wood, but occasionally of nonrusting metal, equipped with large doors for charging and withdrawal of the product. They are designed to turn on the longitudinal axis at about 25–30 r.p.m. and have internal baffles which continuously lift and drop their contents, and thus provide agitation with considerable splashing and concussion. Churns are built in diameters between about 3 and 10 feet. A typical churn will be about 5 feet in diameter and 5 feet long, with an over-all capacity in the neighborhood of 700 gallons. When filled to

[27] L. S. Palmer and H. F. Wiese, *J. Dairy Sci.*, *16*, 41–57 (1933).
[28] H. F. Wiese and L. S. Palmer, *J. Dairy Sci.*, *15*, 371–381 (1932). L. S. Palmer, *ibid.*, *27*, 471–481 (1944). R. Jenness and L. S. Palmer, *ibid.*, *28*, 611–623 (1945).

the usual capacity of about 40% by volume, with 280 gallons of 35% cream, it will yield about 1000 pounds of butter per charge.

The churning operation is judged to be at an end when the granules of butterfat are of about pea size. At this point the churn is stopped, the buttermilk is drained off, and wash water is added equivalent approximately to the buttermilk removed. The wash water must be cold, but should not be excessively so (below about 45°F.). The wash water and butter are given a few revolutions, and the water is drained off; usually only one wash is given before working is started. Workers are ordinarily integral with the churn, although in some models they are separate and are inserted through the end of the churn after the latter is opened. They consist of either two or four rolls shaped with four grooves and four ridges, which are so set that the ridges of one roll loosely engage the grooves of the other. Passage of the butter between the rolls provides a kneading action. In the working operation the water content of the batch is adjusted to the desired value (about 80.5–81.0%). This usually requires that a little water be added. In the finished butter about 65–70% of the total moisture is said to be derived from the cream, with the remaining 30–35% coming from the wash water. Salt is also worked in at this stage.

In Europe there is some use of working tables, onto which the contents of the churn are discharged, but these are seldom seen in the United States. After working, the butter is packaged into tubs, cubes, or prints, the latter being formed and wrapped by automatic machinery.

(c) Continuous Processes

Two new continuous buttermaking processes have recently been patented in this country. Both involve heating of the cream to melt the fat therein completely, separation of the heated material to a fat content in excess of 80%, reconstitution of the high-fat material with milk, water, salt, and color to the legal fat content of 80%, emulsification of the reconstituted mixture, and solidification of the emulsion in a continuous chiller, followed by continuous working and printing. In the Farrall process[29] it is claimed that passage of the high-fat (78%) cream from the initial stage of (centrifugal) separation through a homogenizing valve at high pressure (1100–1300 pounds), followed by gravity separation, will produce a material containing 98% fat, which is then continuously reconstituted with the aid of a proportioning pump. The process patented by Lundal and Robichaux[30] aims only at producing a cream with slightly over 80% fat, which is adjusted to the proper composition batchwise in a series of "standardizing" vats. The Farrall process begins with pasteur-

[29] A. W. Farrall (to Creamery Package Mfg. Co.), U. S. Pat. 2,406,819 (1946).
[30] I. G. Lundal and R. P. Robichaux (to Cherry-Burrell Corp. and Sugar Creek Creamery Co.), U. S. Pat. 2,407,612 (1946).

ized cream, whereas the Lundal-Robichaux process carries out a combined pasteurization and deodorization treatment with steam under reduced pressure on the high-fat material, achieving at the same time some further reduction of the moisture content. It is mentioned in the specification of the Farrall patent that a valve-bowl separator must be used in the initial separation of sour cream (but not of sweet cream) to prevent clogging.

Two continuous processes developed in Germany have been described in recent United States' literature.[31] Of these, the so-called Alfa process resembles those described above, in that the cream is separated to a high-fat content in the first stage of the operation. The Roth or Fritz process employs continuously operating churns and workers on cream of normal fat content, churning being followed by draining off the buttermilk in the usual manner.

(d) Production of Butter Oil

In India, Africa, and other tropical regions butterfat (often from milk other than cows' milk) is commonly marketed and used in a virtually anhydrous form, after separation of the fat from the milk serum by heating and settling. In India the product is known as *ghee*. For details of the manner in which it is prepared and its characteristics reference should be made to the publication of Davies[32] or to other Indian publications.

Since dry butter oil has much better keeping properties than butter, there is some manufacture of this commodity in Australia, New Zealand, and other countries where the dairy industry is highly developed, particularly where it is desired to ship or store the fat for long periods without maintaining it at cold-storage temperatures. Butter, cream, milk, or ice cream may be reconstituted from the oil with fluid milk, skim milk powder, water, etc.

In the manufacture of butter oil unsalted butter is melted, settled by gravity, centrifuged repeatedly, dehydrated under vacuum, cooled, and packed in sealed tins. The modern process has been described in detail by McDowall *et al.*,[33] El Rafey *et al.*,[34] and others.[35,36] The Farrall continuous buttermaking process, described above, is claimed to be adaptable to the manufacture of butter oil.

[31] See, for example, A. V. Gemmill, *Food Inds., 18,* 841–843, 996, 998 (1946); F. H. McDowall, *ibid., 19,* 208–214 (1947).
[32] W. L. Davies, *Indian Indigenous Milk Products,* Thacker, Spink & Co., Calcutta, 1940, pp. 35–60.
[33] F. H. McDowall, R. M. Dolby, E. Beatson, and J. J. O'Dea, *New Zealand J. Sci. Technol., B24,* 53–78 (1942)
[34] M. S. El-Rafey, G. A. Richardson, and J. L. Henderson, *J. Dairy Sci., 27,* 807–820 (1945).
[35] See, for example, *Food Inds., 14,* No. 10, 114 (1942); *ibid., 17,* 370–373, 456–458 (1945).
[36] D. V. Josephson and C. D. Dahle, *Food Inds., 17,* 630–633 (1945).

It has been pointed out by Josephson and Dahle[36] that, whereas heating of pure dry butterfat decreases its stability (resistance toward oxidation), heating of cream or butter prior to extraction of the fat has a beneficial effect on the stability, presumably due to the production of antioxidant sulfhydryl compounds from the milk proteins.

C. Margarine

1. Historical

Margarine was invented during the Franco-Prussian War by the French chemist, Mége-Mouriés. It won for the inventor a prize offered by Napoleon III for a satisfactory butter substitute. The award of the prize was made in 1870. By 1872 the product appears to have attained commercial importance in France, and shortly thereafter it was being produced in a number of other countries, including the United States.

The original process for making margarine involved the following successive steps: (a) the low-temperature rendering of beef fat; (b) fractional crystallization of the rendered fat to yield a fraction of lower melting point than the original fat; and (c) the production of a butterlike flavor by mixing this fraction with milk and digesting the mixture with tissues from cow udders.

The final step was apparently intended to imitate the natural body processes of the cow, in the belief that butterfat was formed from the body fat of the animal by the action of substances present in the udder. This belief was of course in error. No such transformation of fat is possible, and such butterlike flavor as the product possessed could only have been derived from the action of bacteria in the milk. However, the principle of treating fats other than butterfat with milk to produce the flavor of butter was established, even though by accident.

The improvements which were subsequently introduced in the original Mége-Mouriés process have been traced in some detail by Snodgrass.[1] The use of mammary tissues in the preparation of margarine was probably abandoned at a relatively early date. Shortly thereafter it was discovered that a more pronounced flavor of butter could be imparted to the product by souring or ripening the milk before incorporating it with the fat, and the use of previously soured milk became the accepted practice. Eventually it was found that certain strains of milk-souring bacteria produced a more pleasing aroma in butterfat than did others, and the use of pure cultures for ripening cream for butter manufacture became general. When the same cultures were employed for fermenting the milk to be incorporated into margarine, an improvement in the flavor of this product was also obtained. Consequently, the spontaneous souring of the milk was abandoned in favor of controlled fermentation by butter cultures.

The first important improvement in the process, from the standpoint of the physical properties of the product, was the introduction of a method of quickly solidifying the fat, in order to avoid the formation of large crystals, with consequent graininess and poor consistency in the fat. The first method of margarine solidification involved simply running the emulsion of milk and liquid fat in a slow stream into a vat of chilled water. This method was in vogue for many years, and it is only quite recently that it has been largely replaced by the chill roll and closed chiller methods of solidification, in which the fat is crystallized by contact with a refrigerated metal surface.

According to Snodgrass,[1a] the techniques of employing both rapid crystallization and previously soured milk were first described by Mott, in the United States, and were in commercial use in this country as early as 1877.

Milk in combination with fat alone does not have a sufficient content of surface-active materials to produce an emulsion of the same stability as that existing in butter. Much of the literature on margarine manufacture pertains to the use of various added substances to promote emulsification. Margarine which contains insufficient emulsifying agents not only is inclined to be "leaky" in storage, but also does not behave properly in cooking. Its deficiencies in comparison with butter are particularly noticeable in frying, where the ready separation of its water and fat phases causes the margarine to spatter, and also causes the curd or milk solids to adhere to the frying pan.

Probably the first added emulsifying agent to be used in margarine in any quantity was egg yolk. A German patent covering the use of this material was granted in 1884.[1a] Since the introduction of the Bollman process[37] for the production of relatively cheap vegetable phosphatides from soybeans, however, vegetable lecithin has largely replaced egg yolk. The addition of glucose to margarine to produce foaming and browning is said to be common in Europe. In the United States, large quantities of synthetic emulsifying agents, such as mono- and diglycerides, and sodium monostearin sulfoacetate, are used.

In margarine solidified by the modern continuous process in closed chilling machines a very fine dispersion of the aqueous phase may be obtained, which practically eliminates "leaking" or "weeping" of the product even in the entire absence of an emulsifying agent. An antispattering agent is desirable in such margarine, however.

Inasmuch as the chief nutritional deficiency of ordinary fats, as compared with butterfat, resides in their negligible content of vitamin A, it is natural that margarine manufacturers should have given consideration to the addition of concentrates of this vitamin to their products. The addi-

[37] H. Bollman, Brit. Pat. 259,166 (1925).

tion of both vitamins A and D to margarine has been practiced in Europe for some years, but until quite recently such addition was illegal in the United States. In 1941 a ruling of the Federal Security Administration permitted the addition of vitamin A equivalent to its normal content in butter, and since that time most of the margarine marketed in the United States has contained 15,000 U.S.P. units of this vitamin per pound.

2. MARGARINE LEGISLATION

The invention of margarine made it possible to prepare a product very similar to butter from oils and fats which are much less expensive than butterfat. Hence the trade in margarine offers peculiar opportunity for the practice of fraud upon the consumer, who may be sold margarine under the impression that he is being supplied with butter. At the same time, the sale of margarine under any circumstances may be considered inimical to the interests of the dairy industry because of the relative cheapness with which it can be manufactured. These two considerations have given rise to much legislation governing the production and distribution of margarine.

Other federal legislation which affects the manufacture of margarine very broad, and embraces any plastic fat composition emulsified with moisture in excess of 1%, with the exception of water-churned puff-paste shortening, which is specifically exempted from the provisions of the act, provided that its melting point is in excess of 118°F.

Other federal legislation which affects the manufacture of margarine includes the Federal Food, Drug, and Cosmetic Act. This act provides for the establishment of a definition of margarine, in terms of its various ingredients, and forbids the use of ingredients not specifically included in the definition. The definition and standard of identity for margarine, as promulgated by the Federal Security Administration, June 15, 1941, under the provisions of the Federal Food, Drug, and Cosmetic Act, is as follows:

(a) Oleomargarine is the plastic food prepared with one or more of the optional fat ingredients named under one of the following subparagraphs (1), (2), (3), or (4):

(1) The rendered fat, or oil, or stearin derived therefrom (any or all of which may be hydrogenated), of cattle, sheep, swine, or goats, or any combination of two or more of such articles.

(2) Any vegetable food fat or oil, or stearin derived therefrom (any or all of which may be hydrogenated), or any combination of two or more of such articles.

(3) Any combination of ingredients named under subparagraphs (1) and (2) in such proportion that the weight of the ingredients named under (1) either equals the weight of the ingredients named under (2), or exceeds such weight by a ratio not greater than 9 to 1.

(4) Any combination of ingredients named under subparagraphs (1) and (2) in such proportion that the weight of the ingredients named under (2) exceeds the weight of the ingredients named under (1) by a ratio not greater than 9 to 1.

One of the five following articles is intimately mixed with the fat ingredient or ingredients, after such article has been pasteurized and subjected to the action of harmless bacterial starters: (*i*) cream, (*ii*) milk, (*iii*) skim milk, (*iv*) any combination of dried skim milk and water in which the weight of the dried skim milk is not less than 10 percent of the weight of the water, or (*v*) any mixture of two or more of these. (The term "milk" as used herein means cow's milk.) Congealing is effected, either with or without contact with water, and the congealed mixture may be worked. In the preparation of oleomargarine one or more of the following optional ingredients may also be used:

(*5*) Artificial coloring.

(*6*) Sodium benzoate, or benzoic acid, or a combination of these, in a quantity not to exceed 0.1 percent of the weight of the finished product.

(*7*) Vitamin A, added as fish liver oil or as a concentrate of Vitamin A from fish liver oil (with any accompanying Vitamin D and with or without added Vitamin D concentrate), in such quantity that the finished oleomargarine contains not less than 9,000 United States Pharmacopoeia Units of Vitamin A per pound.

(*8*) The artificial flavoring diacetyl added as such, or as starter distillate, or produced during the preparation of the product as a result of the addition of citric acid or harmless citrates.

(*9*) (*i*) Lecithin, in an amount not exceeding 0.5 percent of the weight of the finished olemargarine, or (*ii*) monoglycerides or diglycerides of fat-forming fatty acids, or a combination of these, in an amount not exceeding 0.5 percent of the weight of the finished oleomargarine, or (*iii*) such monoglycerides and diglycerides in combination with the sodium sulfo-acetate derivatives thereof in a total amount not exceeding 0.5 percent of the weight of the finished oleomargarine, or (*iv*) a combination of (*i*) and (*ii*) in which the amount of neither exceeds that above stated, or (*v*) a combination of (*i*) and (*iii*) in a total amount not exceeding 0.5 percent of the weight of the finished oleomargarine. (The weight of diglycerides in each of ingredients (*ii*), (*iii*), (*iv*), and (*v*) is calculated at one-half actual weight.)

(*10*) Butter.

(*11*) Salt.

The finished oleomargarine contains not less than 80 percent fat, as determined by the method prescribed in "Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists," 4th Edition, 1935, page 289, or 5th Edition, 1940, page 298, under "Indirect Method—Official."

(*b*) When any ingredient named under one of the following specified subparagraphs of paragraph (*a*) is used, the label shall, except as hereinafter provided, bear the statement set forth below after the number of such subparagraph:

Subparagraph (*1*): "Prepared from Animal Fat," or "Made from Animal Fat."

Subparagraph (*2*): "Vegetable," or "Prepared from Vegetable Fat," or "Made from Vegetable Fat."

Subparagraph (*3*): "Prepared from Animal and Vegetable Fats," or "Made from Animal and Vegetable Fats."

Subparagraph (*4*): "Prepared from Vegetable and Animal Fats," or "Made from Vegetable and Animal Fats."

Subparagraph (*5*): "Artificially Colored", or "Artificial Coloring Added," or "With Added Artificial Coloring."

Subparagraph (*6*): "Sodium Benzoate (or, as the case may be, 'Benzoic Acid' or 'Sodium Benzoate and Benzoic Acid') Added as a Preservative," or "With Added Sodium Benzoate (or, as the case may be, 'Benzoic Acid' or 'Sodium Benzoate and Benzoic Acid') as a Preservative."

Subparagraph (7): "Vitamin A Added," or "With Added Vitamin A."

Subparagraph (8): "Artificially Flavored," or "Artificial Flavoring Added," or "With Added Artificial Flavoring."

Where oil is used, the word "oil" may be substituted for "fat" in the label statement. In lieu of the word "animal" or "vegetable" in any such statement, the common or usual name of the fat ingredient subparagraphs (5), (6), (7), (8) are used, the words "added" or "with added" need appear only once, either at the beginning or end of the list of such ingredients declared. The declaration of Vitamin A may include the number of United States Pharmacopoeia Units which have been added.

Whenever the name "oleomargarine" appears on the label so conspicuously as to be easily seen under customary conditions of purchase, the words and statements here prescribed showing ingredients used shall immediately and conspicuously precede or follow, or in part precede and part follow, such name, without intervening written, printed, or other graphic matter.

Discriminatory legislation which placed federal excise taxes of 0.25 cent per pound on uncolored, and 10 cents per pound on colored, margarine, plus license fees for manufacturers, wholesalers, and retailers, was repealed early in 1950. However, a number of the states still impose heavy taxes on the product, and some prohibit the sale or manufacture of colored margarine outright.

3. FLAVOR

The flavor of good margarine is very similar to, but not altogether identical with that of butter. Properly speaking, none of the natural flavors of fats and oils has any place in margarine. It is desirable for margarine fat to be completely neutral. Carefully rendered oleo oil or neutral lard is sufficiently free from flavor to be reasonably suitable for margarine, although now it is not uncommon for even these fats to be deodorized, in some cases after slight hydrogenation, before they are used for this purpose. It is necessary for vegetable oils to be very completely deodorized for margarine manufacture as their natural flavor is more foreign to this product than is that of the animal fats mentioned above.

Coconut oil and the other oils of the lauric acid type are flavorless when properly deodorized and are stable toward oxidation, hence are entirely suitable margarine fats. Otherwise, the oils which may be hydrogenated for the production of good margarine fats are the ones which are likewise suitable for the manufacture of high-grade all-hydrogenated shortenings. Cottonseed, peanut, sesame, sunflower, and other liquid oleic-linoleic acids oils may be used in margarine in practically any combination or in any proportions. Hydrogenated soybean oil contributes a slight foreign flavor to the product if it is present to the extent of more than 25 to 30%. Other oils of the linolenic acid group are relatively poor margarine oils, as is rapeseed oil. Fish oils are not suitable materials for the preparation of

hydrogenated margarine fats, as they invariably revert in flavor except when hydrogenated virtually to the form of stearine. Hydrogenated whale oil is greatly superior to fish oil, and is much used in margarine manufacture in Europe. Data relative to the actual procedure followed in hydrogenating whale oil for this purpose are unavailable, but it may be assumed that much care must be exercised to avoid excessive flavor reversion in this oil also.

Much of what has been said previously regarding the flavor of butter is also applicable to margarine. The same bacterial cultures are used for preparing milk for margarine manufacture as are employed in the ripening of cream for buttermaking, and it is probable that the reactions which take place are quite similar. Lately, the addition of diacetyl (up to ca. 3 p.p.m.) or other flavoring material to supplement natural flavors has become a common practice among margarine manufacturers.

4. Consistency

There is perhaps no plastic fat product in which the matter of consistency is of such importance as in margarine. One essential qualification of table margarine is that it shall melt readily and with practical completeness in the mouth. In this respect there is an essential difference between margarine and shortenings. Whereas shortenings are invariably consumed in the molten form, in various hot dishes, or else finely dispersed in pastries, etc., margarine, like butter, is for the most part spread on bread and taken into the mouth in more or less gross portions. A residue which fails to melt at body temperature may not be noticeable in a shortening—in fact, such a residue is necessary if the product is to have high-temperature body—but in margarine it imparts an undesirable "pasty" sensation in the mouth.

At ordinary temperatures, margarine should be plastic and should spread freely. At refrigerator temperatures, however, it should be reasonably firm, to permit it to be easily formed into the 1-pound or 0.25-pound prints in which it is customarily marketed.

In general, the consistency and melting characteristics of good brands of margarine resemble those of butter (Table 75). However, there is a considerable difference in the consistency of European margarine, which is like that of soft summer butter, and usually melts completely well below body temperature, and American margarine, which resembles relatively firm butter, and barely melts below the temperature of the human body. The general endeavor of American manufacturers to avoid excessive pastiness in the mouth, and yet retain maximum body in the range of 85–90°F. derives from the widespread practice in retail stores of displaying the product without refrigeration, which requires it to withstand

severe summer temperatures without melting and running from the package. Needless to say, this practice is undesirable in every respect; it not only causes much American margarine to be excessively high melting, but also is injurious to the flavor stability. The sample of American margarine of Table 75 may be considered one of relatively good body; products which have considerably more high-temperature body and are noticeably pasty are not uncommonly encountered.

The consistency of margarine is principally dependent upon the fats used in its manufacture and is influenced comparatively little by ordinary variations in methods of solidifying and emulsifying the product, or by variations in the relative proportions of milk and fat.

Where such ingredients as oleo oil, oleo stock, neutral lard, coconut oil, palm kernel oil, babassu oil, etc., are used in preparing the margarine fat, the proper consistency is obtained by blending the various fats in the proper proportions. If the fat is to be prepared by the hydrogenation of a normally liquid oil, however, the more usual practice is to attain the proper consistency by a single, carefully controlled hydrogenation. American manufacturers sometimes blend a minor proportion (10–20%) of liquid oil with a stock hydrogenated to a consistency slightly too firm for use alone, but otherwise the practice of blending fats of different degrees of hardness is not generally considered advantageous in the manufacture of margarines. In such margarine it is a matter of some difficulty to hydrogenate the oil to a sufficient degree of firmness at low temperatures without exceeding the desired melting point, and mixtures or blends of hydrogenated oils are invariably less satisfactory in this particular than a single hydrogenated oil.

The foregoing considerations apply, of course, only to table margarine. Pastry margarines, which are used for cooking, are not required to melt at body temperature. Margarines of the puff-pastry type are, in fact, the highest melting of all edible fat products. The puff-pastry fat most commonly sold in the United States is made from 35% oleostearine blended with 65% cottonseed oil, and has a melting point in excess of 118°F. A tough, waxy body is essential in this product, in order to make it extensible in the "rolling in" process used in making puff pastry.

5. Ingredients

(a) Fats

Preference for margarine fats in the United States is now in the third of three well-defined stages.

As noted previously, the first margarine was made from oleo oil, prepared by the fractional crystallization of beef fat. Oleo oil is by itself

quite similar in physical properties to butter. It is firm at low tempera-
tures, and yet, like butter, it melts readily in the mouth. Later, oleo oil
was supplemented by neutral lard, which in reasonable proportions oc-
casioned no harm to the body of the product, or even improved it, by
slightly extending its plastic range. For many years these two animal
fats continued to be the principal raw materials used in margarine manu-
facture. Vegetable oils were little used, partly because most of them were
too soft to be included in margarine in any quantity, and partly because
refining and deodorizing processes were not sufficiently developed to
permit the production of a fat with a neutral flavor from vegetable mate-
rials.

During the years 1914 to 1919, deodorized coconut oil began to be much
used in margarine. Coconut oil, palm kernel oil, babassu oil, etc., are
somewhat more brittle than oleo or mixtures of oleo oil and neutral lard,
at the lower temperatures, and also have a somewhat lower melting point.
However, if their plastic range is extended somewhat, by the inclusion of
minor proportions of a liquid oil, and oleo stock, oleostearine, or hydro-
genated oil, they have a suitable consistency for margarine manufacture.
The use of coconut oil increased rapidly, and by 1929 this oil constituted
over 60% of the total fats and oils used in the industry.

Since about 1934, the relative volume of coconut oil consumed by the
margarine industry has declined, and there has been a corresponding in-
crease in the use of hydrogenated cottonseed and soybean oils. This latter
shift in raw materials may be attributed in part to the imposition of new
federal processing taxes on coconut and other foreign oils in 1934, and in
part to a general advance in oil and fat technology. Previously, cotton-
seed, soybean, and similar oils had been used to some extent in margarine,
but seldom as the sole or principal fatty ingredients of the product. Al-
though fats suitable for the manufacture of shortenings had been prepared
from such oils for many years by hydrogenation, it was not recognized
that fat of the proper consistency for margarine could be prepared by
hydrogenation of a liquid oil. Subsequent experience demonstrated that the
body of properly prepared hydrogenated products was even superior to
that of margarine made from oleo oil, coconut oil, or other natural fats.
In addition, hydrogenation permits the manufacture of fats which are
very stable, neutral in flavor, and highly uniform in consistency. At the
present time, most of the margarine of the highest grade made in the
United States is a hydrogenated vegetable oil product.

The changes in the fats used in margarine in the United States during
the past thirty years are indicated in Table 76.

In many respects, the trend of consumption of the various fats has
run a parallel course in Europe. There, too, the use of animal fats has
declined greatly from its previous high point. Prior to 1914, oleo oil ex-

ported from the United States was one of the major ingredients of European margarine. In 1908, exports of oleo oil for this purpose reached a record volume of 212,000,000 pounds. After 1924, however, exports declined to less than 100,000,000 pounds yearly, and since 1934 they have not exceeded 10,000,000 pounds in any one year.

Coconut, palm kernel, and babassu oils were used in large quantities in Europe before they became very popular in the United States. The large-

TABLE 76

FATS AND OILS USED IN MANUFACTURE OF MARGARINE IN UNITED STATES IN SPECIFIED YEARS (PERCENTAGES OF TOTAL)

Fat	1917	1922	1927	1932	1937	1942	1948
Oleo oil................	40.3	25.7	20.9	7.5	3.8	6.5	0.6
Neutral lard............	17.7	16.9	10.5	5.6	0.6	2.3	0.5
Other animal fats.......	2.5	4.8	4.2	2.5	1.4	2.0	0.5
Total animal fats........	*60.5*	*47.4*	*35.6*	*15.6*	*5.8*	*10.8*	*1.6*
Coconut oil.............	8.2	35.7	51.7	73.7	22.6	1.0	0.7
Cottonseed oil..........	26.6	9.6	10.4	9.0	53.2	48.0	61.6
Soybean oil.............	—	—	—	—	9.8	38.4	34.4
Other vegetable oils.....	4.7	7.3	2.3	1.7	8.6	1.8	1.7
Total vegetable oils......	*39.5*	*52.6*	*64.4*	*84.4*	*94.2*	*89.2*	*98.4*

scale use of hydrogenated cottonseed, soybean, and peanut oils in Europe also antedated the use of these oils in the United States. Manchurian soybean oil, in particular, was imported into Germany in large quantities prior to 1914, and was principally consumed by the margarine industry.

In later years hydrogenated whale oil came to be the most important single ingredient of European margarine. Probably much more than half of the annual whale oil production of about 1,250,000,000 pounds was regu-

TABLE 77

OILS AND FATS (MILLIONS OF POUNDS) USED IN PRODUCTION OF MARGARINE IN UNITED KINGDOM AND GERMANY

Oil or fat	United Kingdom (1937)	Germany[a] (1935)
Whale oil...........................	148	470
Beef fat.............................	18	11
Hog fat.............................	2	4
Cottonseed oil.......................	31	—
Peanut oil...........................	69	29
Soybean oil..........................	0	60
Coconut oil..........................	60	99
Palm kernel oil......................	22	126
Other oils...........................	11	69

[a] Includes about 10% of edible fats not used in margarine.

larly used for this purpose. Among the other fats and oils, palm kernel oil has been particularly favored in Germany, whereas British margarine manufacturers have been more inclined to the use of cottonseed and peanut oils. The oils and fats used in the United Kingdom and Germany in typical years prior to 1939 are listed in Table 77.

Typical formulas for three grades of European margarine are given by Thornley et al.[37a] as follows:

Oil	Grade A	Grade B	Grade C
Palm kernel.................	320	350	310
Coconut...................	370	340	336
Hydrogenated peanut........	100	50	—
Peanut....................	200	150	—
Hydrogenated whale..........	221	221	365
Soybean...................	—	50	200

The only fats which are used in margarine without processing treatment are neutral lard, and oleo stock and its derivatives, oleo oil and oleostearine. In order to be suitable for margarine, these fats must be rendered and subsequently handled with extreme care. Only very fresh fatty tissues can be rendered, and the rendering operation must be carried out at a low temperature in order to avoid the production of oxidized or cooked flavors in the expressed fat. After the fat is prepared, it should be made up into margarine with reasonable promptness. The flavor of neutral pork and beef fats is very easily damaged by slight oxidation, and prolonged storage or repeated melting or heating of the fats during storage or processing is extremely detrimental to their quality. These fats are most successfully handled by meat-packing plants which are engaged in both rendering and margarine-manufacturing operations, so that the fats can be promptly transferred from one department to the other.

Since processing facilities for hydrogenation and deodorization have become more generally available, it has become quite common practice to subject animal fats to alkali refining and slight hydrogenation, followed by deodorization, before they are incorporated into margarine. This practice enables the manufacturer to utilize fats which have been stored or have otherwise slightly deteriorated in flavor, and results in a product which is markedly superior in stability to margarine made from even the highest grade unhydrogenated fats. Deodorization of these fats is much more successful if it is preceded by hydrogenation; the flavor is inclined to be unstable if they are deodorized without previous treatment.

In preparing margarine oil from cottonseed, soybean, and other liquid

[37a] T. Thornley, R. Delarageaz, and A. Arneil, *Technical Developments in the German Margarine Industry*, Report No. 274. Items 21, 22. British Intelligence Objectives Subcommittee. H. M. Stationery Office, London.

oils by hydrogenation, the process should be carried out under highly selective conditions, in order to harden the oil properly without producing in it an excessive amount of fully saturated, high melting glycerides. If the hydrogenation is not carried out properly, an oil with the proper melting point and high-temperature consistency will be too soft to print properly, and conversely, an oil which is sufficiently firm at 40° to 60°F. will be pasty in the mouth.

Efficient, high-temperature deodorization is necessary for oils or hydrogenated oils of the oleic-linoleic acid type which are to be used in margarine.

Coconut oil or other oils of the lauric acid type are, like the oleic-linoleic acid oils, refined and deodorized for margarine manufacture, but are not usually hydrogenated. These oils are best blended with a certain proportion of both soft oils and hard fats, to improve their plastic range, because alone they soften and melt too abruptly.

Pastry or cooking margarines may be prepared from a somewhat greater variety of materials than ordinary table margarines, because in these products it is not necessary for the fat to melt cleanly in the mouth. The consistency of these margarines covers a considerable range, according to the preferences of the particular trade for which they are designed, and is controlled by suitably varying the proportions of the various fatty ingredients or the conditions of the hydrogenation process. Puff-paste fat, which in the United States is not officially designated as a margarine because of its high melting point (over 118°F.), is usually made by compounding 35% oleostearine with 65% deodorized cottonseed oil and emulsifying this fat with 6 to 8% water. The oleostearine may be replaced by a vegetable oil or other softer oil hydrogenated to the approximate consistency of oleostearine, although products made in this fashion are generally considered somewhat lacking in waxiness and less satisfactory than the oleostearine product.

(b) Milk

In the United States skim milk is usually used for margarine manufacture, although a few processors prefer whole milk, claiming that it produces a product of better flavor. Milk reconstituted from powder can be used, though its use is practically restricted to the few localities that lack a dairy industry.

It is preferable for the milk to be raw, rather than pasteurized, upon arrival at the margarine plant, and its acidity must be low, i.e., not over 0.1%, or at the most 0.2%.

(c) Surface-Active Materials

As mentioned previously, it is necessary to add special emulsifying agents to margarine in order to confer upon it the physical properties of the butter emulsion. Margarine prepared without the use of added agents is inclined to "leak" or exude the aqueous phase while in storage, unless manufacturing methods have been employed which yield a very tight emulsion. Also, when used in cooking, and particularly in frying, the behavior of untreated margarine is quite different from that of butter.

The emulsifying agents naturally present in butter effectively prevent the coalescence of water droplets even after the emulsion is heated. Under these circumstances, the volatilization of water in the frying process occurs from a multitude of very small droplets, with the appearance of quiet foaming, and without the milk solids settling to the bottom of the frying pan. In margarine, however, unless added emulsifying agents are present, there will be a marked tendency for the small droplets to unite to form large drops upon the application of heat. The generation of steam from such large drops is sufficiently violent to eject particles of oil from the cooking vessel and cause spattering. Also, the milk solids or curd tend to settle out of the aqueous phase and become adherent to the bottom of the vessel.

A wide variety of substances has been suggested for addition to margarine to improve its emulsifying properties. The use of egg yolk for this purpose was probably quite common in Europe at one time. Lately, however, it has been more or less completely supplanted by soybean lecithin.[37-39] Lecithin has never been quite as popular in the United States as in Germany and other European countries, although nearly 1.5 million pounds (an average of 0.7%) was reported used in 1948–49. Lecithin is usually added in an amount not exceeding 0.5% of the weight of the fat.

Another emulsifying agent which has been considerably used, especially in Europe, is the so-called "Paalsgaard emulsion oil" of Schou,[40] which consists of soybean oil that has been oxidized and polymerized for the production of hydrophilic groups.

The present tendency in the United States is toward the use of lecithin in combination with synthetic surface-active agents prepared from a glyceride or fatty acid base. Ordinary mono- and diglycerides as prepared for incorporation into superglycerinerated shortenings, are quite effective "antileaking" agents in a concentration of a few tenths of one percent,

[38] Hanseatische Mühlenwerke A.-G., German Pat. 576,102 (1933).
[39] B. Rewald, U. S. Pat. 1,895,424 (1933).
[40] E. V. Schou, Brit. Pats. 187,298–99 (1921). U. S. Pat. 1,570,529 (1926).

but have little if any effectiveness as "antispattering" agents. The sodium sulfoacetate derivatives of the mono- and diglycerides, however, are very effective antispattering agents, and are widely used as such.

The effectiveness of the latter class of substances in preventing spattering is explained by Harris[41] on the basis of a proper balance between hydrophilic and lipophilic groups in the molecule.

The various synthetic substances (with the exception of monostearine) are classified together by the Bureau of Internal Revenue as "glycerine derivatives," of which 1,323 thousand pounds were consumed in 1948–49, in the manufacture of 827,540 thousand pounds of margarine. During the same year there was a consumption of 725 thousand pounds of monostearine.

(d) Other Ingredients

The salt used in margarine is a special flake grade manufactured for dairy use, in which the crystals are small and easily dissolved, and which is low in pH and in calcium and magnesium compounds. The saltiness of

TABLE 78

MATERIALS USED IN MANUFACTURE OF MARGARINE IN UNITED STATES DURING YEAR ENDING JUNE 30, 1949[a]

Material	Pounds	Per cent of total
Cottonseed oil	435,250,470	49.88
Soybean oil	244,543,635	29.03
Neutral lard	4,118,804	0.47
Peanut oil	4,008,747	0.46
Oleo oil	3,507,368	0.40
Oleostearine	3,057,775	0.35
Corn oil	1,539,264	0.18
Coconut oil	890,314	0.10
Oleo stock	496,115	0.06
Soybean flakes	20,297	0.002
Milk	144,400,995	16.55
Salt	26,288,924	3.01
Lecithin	1,457,951	0.17
Glycerin derivatives	1,323,127	0.15
Monostearin	724,945	0.08
Sodium benzoate	596,176	0.068
Vitamin concentrates	167,889	0.019
Color	86,658	0.0099
Butter flavor	58,014	0.0066
Diacetyl	3,477	0.0004
Total	*872,540,945*	*100.00*

[a] Bureau of Internal Revenue report.

[41] B. R. Harris, U. S. Pats. 1,917,249–60 (1933).

the margarine depends not only upon the total amount of salt present, but also upon the fineness with which the aqueous phase is dispersed. At a given salt concentration very fine emulsions taste considerably less salty than coarse ones. American margarine may be considered to have an average salt content of about 3.0% with extremes of perhaps 2.25% and 4.0%.

In addition to the materials mentioned previously, the ingredients commonly used in margarine include sodium benzoate, which is in some cases added to the aqueous phase as a preservative, and vitamin A concentrates which are added to the fat to the amount usually of 15,000 U.S.P. units per pound, to improve its nutritive qualities. The degree to which the various minor ingredients of margarine are used in the United States is indicated in Table 78, covering the materials reported by the Bureau of Internal Revenue during 1948–1949.

6. Margarine Manufacture[41a]

(a) Preparation of the Milk

As stated previously, the flavor and aroma of margarine depend to a large extent upon the treatment of the milk used in its manufacture. Only the best bacterial cultures, with proved flavor- and aroma-producing qualities should be used in ripening the milk. As the proper care and maintenance of a culture involves, in effect, the husbandry of countless successive generations of bacteria, it is not a simple matter. Apparently quite similar strains of bacteria differ markedly in their ability to produce diacetyl and other substances causing desirable flavors, and a culture may lose its good qualities through attenuation or contamination with undesirable organisms. The mother culture should be periodically checked for stray organisms by microscopic examination, and the ability of the bacteria to produce acetylmethylcarbinol and diacetyl should be confirmed by application of the creatine test[5] or other suitable tests. It should be noted that the flavor and odor of the culture or starter itself is not an altogether satisfactory indication of its ability to develop a pleasing flavor, as prior to emulsification with the fat the desired substances may be largely in the form of acetylmethylcarbinol, which is relatively flavorless and odorless, rather than diacetyl.

A supply of cultured milk in quart bottles is maintained by daily inoculations followed by incubation of the milk at about 70°F. for 16–18 hours. While the original cultures are sometimes carried along for months or even years at the margarine plant, it is better practice to have a new

[41a] For a recent review of British practice in margarine manufacture, see M. K. Schwitzer, *Ind. Chemist*, *25*, 349–358 (1949). For reviews of American practice, see A. A. Robinson, *Oil & Soap*, *15*, 203–206 (1938); J. E. Slaughter, Jr., and C. E. McMichael, *J. Am. Oil Chem. Soc.*, *26*, 623–628 (1949); L. C. Brown, *ibid.*, *26*, 632–636 (1949).

culture supplied about every two weeks by one of the laboratories special-
izing in their selection and propagation.

So-called "starter" is prepared by pasteurizing milk in a starter vat
of about 60–120 gallons capacity, adding to each 60 gallons of the milk
one quart of the culture referred to above, and allowing fermentation to
take place overnight at about 70°F. In the process the acidity rises usually
to 0.7–0.9%.

Milk may be received at the plant in cans, tank cars, or tank trucks.
It is pasteurized either in flash pasteurizers or directly in the milk vats,
which are jacketed and agitator-equipped tanks, usually holding about
500 gallons. For the best results, it is recommended that the milk be
ripened overnight (15–18 hours) at about 60°F., although in some plants
ripening is conducted for a shorter time at a higher temperature (70° or
even 80°F.). Under the former conditions, about 3% of starter is re-
quired, and the acidity may be expected to rise to 0.5–0.6%. At the end of
the ripening period the batch is cooled as rapidly as possible, with agita-
tion, to 35–40°F.

(b) Blending of Ingredients

Scale tanks should be used for accurately proportioning the ingredients
if the emulsion is made up in batches. The salt and any sodium benzoate,
etc., is, of course, dissolved in the milk, whereas the vitamin concentrate
and usually any flavoring materials are added to the oil. Emulsifying
agents may be mixed into either oil or fat, according to their solubility.
Lecithin or monoglyceride preparations are oil-soluble, whereas emul-
sifiers of the sodium sulfoacetate type are water-soluble and are added
to the milk.

The emulsifying tanks must be equipped with efficient agitators. They
are first charged with oil at a temperature somewhat above that desired
in the emulsion (usually 115–120°F.) and the cold milk is slowly added,
at such a rate that no localized cold spots will be produced to cause
crystallization of the oil. A water-in-oil emulsion is formed.

There are some variations of the above procedure. If solidification is
carried out in the Votator chiller the oil and aqueous phases may be
separately fed by proportioning pumps and mixing and emulsification
accomplished in the chilling cylinders. When the continuous proportion-
ing system is used it is preferable to premix at least 2–5% of the milk
into the oil, to avoid the possibility of forming small translucent milk-
free fat particles. If it is desired to incorporate part of the ripened milk
in a salt-free condition, to permit a maximum degree of bacterial action
after the emulsion is formed and concurrently produced a coarser emulsion
than is given by the above method, about 25% of the milk and all of the

oil may be solidified through the Votator machine in the usual way, and the remaining 75% of the milk and all the salt incorporated in the solidified material in the so-called "B-unit" or continuous worker.

This method of incorporating the milk produces in effect two intermixed dispersions of the aqueous phase. One consists of a very finely dispersed system of unsalted milk; the other consists of a relatively coarse system of salted milk. The fine emulsion of unsalted milk presents a sufficient interface to the fat for the adequate development of butterlike flavors, while the coarse emulsion containing the bulk of the milk carries the salt flavor and gives the margarine the appearance and the slightly wet surface customarily found in coarsely emulsified margarines.

If the second portion of milk is chilled to a low temperature, increase in the temperature, due to heat of crystallization, is minimized.

In the European literature on margarine manufacture elaborate directions are to be found for forming emulsions of the proper structure and stability before the material is solidified.[41b] In the American industry, where solidification is almost invariably accomplished in the closed Votator machines, the production of a fine-grained emulsion constitutes no problem, and the object of the preliminary blending of milk and oil is actually only to insure that the proper proportions of the two phases are delivered to the chilling machines.

(c) Solidification. Working and Printing

Three different methods are in use or have been used for solidifying the emulsion of milk and liquid fat. Formerly, the most common method involved continuously pouring or spraying the emulsion into a trough or vat of cold, running water. The emulsion entered at one end of the vat and, as it passed to the other, it solidified and floated to the surface of the water in the form of flaky masses, which were then skimmed off. This method resulted both in washing out a portion of the milk and occluding portions of the cooling water, so that the moisture content of the solidified product was somewhat uncertain. The cooling water was, furthermore, a possible source of bacterial contamination, and was wasteful of refrigeration, since large volumes of water had to be discharged to the sewer without the abstraction of more than a minor part of the refrigeration supplied to it.

The various shortcomings of the refrigerated water system led to the widespread adoption in later years of the chill roll for solidifying margarine. The application of the roll to margarine solidification is not essentially different from its application to the solidification of shortening; the emulsion is chilled by contact with the exterior surface of a revolving,

[41b] See, for example, W. Clayton, *The Theory of Emulsions and Their Technical Treatment*, 4th ed., Blakiston, Philadelphia, 1943.

internally refrigerated drum. The disadvantages of the roll are the same in the case of both products, *i.e.*, the chilling surface and the product are both exposed to the atmosphere. Thus there is opportunity for air-borne contamination of the product, and a considerable amount of refrigeration is lost to the surrounding air.

In plants employing either the cold water or roll method of solidification, it is customary to transfer the solidified emulsion to trucks and hold these for a considerable period of time (24 to 48 hours) in a tempering room at a relatively low temperature before further processing the material. This holding period serves to bring the fat to the proper consistency for working and printing, and also allows opportunity for further bacterial action to take place before the product is salted.
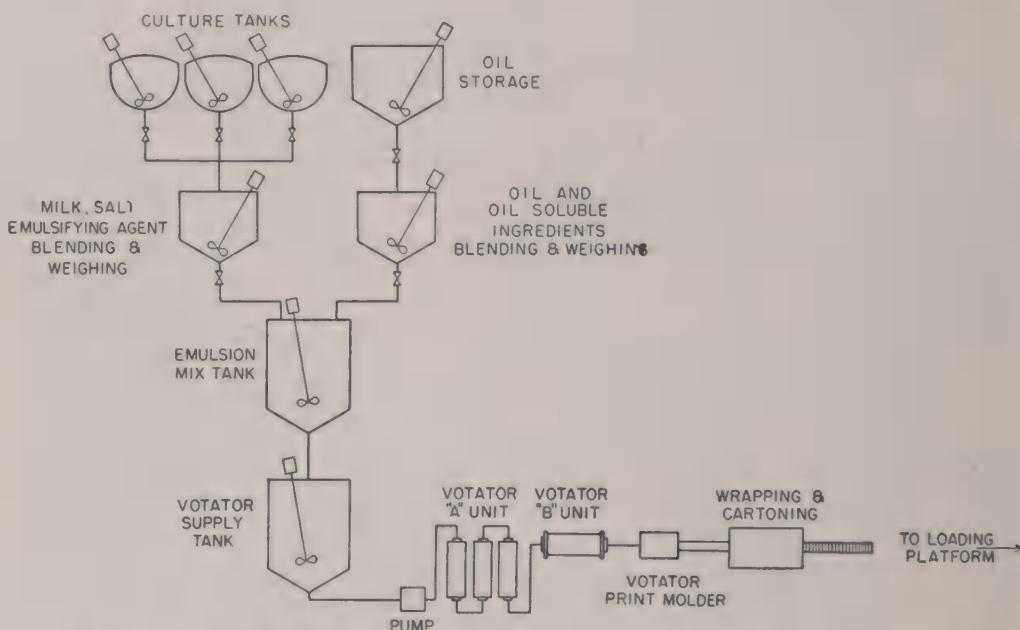
Fig. 35. Simplified flow diagram for continuous margarine solidification.[41d]

After tempering, the material is worked through milling rolls or other machines of various designs and salted. There then remains but the operation of forming it into prints and wrapping and packaging the individual prints. The forming is commonly performed by special automatic print formers which take the blended mass, form it into prints of the desired shape and size, and discharge the prints onto a moving belt. The blocks are mechanically wrapped in parchment or foil and enclosed in cardboard packages. A small envelope of powdered, oil-soluble yellow dye, sufficient in amount to color the print the proper shade of yellow, is attached to the wrapper of uncolored prints.

In some plants the solidified and tempered material is extruded by a

screw press through a perforated plate before the prints are formed. This is designed to avoid the production of an absolutely homogeneous fat, and thus simulate the slightly granular texture of butter and avoid a "salvy" product.

Within recent years, there has been almost unanimous adoption by the American margarine industry of the continuous Votator system of manufacture (see Chapter XXIII). With this system, solidification, tempering, working, etc., are carried out in continuous flow through an enclosed
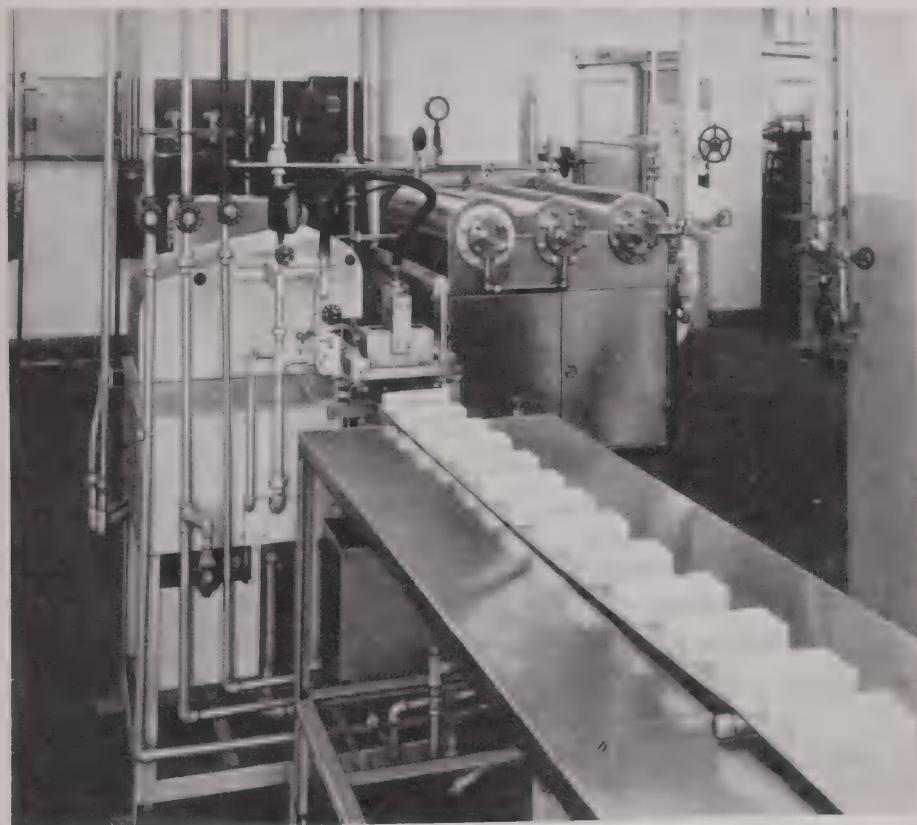
Fig. 36. Continuous margarine solidification machinery. Votator chiller is in right background; print molder and conveyor belt for prints in foreground. (*Courtesy The Girdler Corp.*)

system, with complete protection of the product from atmospheric contamination, highly efficient utilization of refrigeration, positive control of the proportions of all ingredients, elimination of all hand labor, and virtually no waste or recycling of product. Some processors, however, and particularly European processors, feel that the texture of the product is not fully equivalent to that produced by the older method involving long alternate periods of "resting" and working, and that it resembles

that of butter to a lesser extent. However, the continuous method appears to be finding increasing favor abroad.

Recently, much of the uncolored margarine produced in the United States has been packaged in the so-called Peters bag.[41c] This is a pliable and transparent container with a color capsule attached to the inside wall, in which the coloring of the margarine is carried out by kneading the bag and contents before the latter is opened. Margarine to be put up in these bags must be softer than the product which is printed, and is filled much like lard or shortening.[41d]

7. DETERIORATION

Margarine is subject to a number of varieties of deterioration. As in the case of butter, true oxidative rancidity in margarine is rare, although an objectionable degree of flavor reversion may occur. The margarine fat which is perhaps most likely to develop to a serious degree off-flavors from oxidation is oleo oil. Hydrogenated soybean oil will exhibit the same slight degree of flavor reversion in margarine as in shortenings, even though the margarine may be kept under strict refrigeration. So-called "soapiness" in margarine is peculiar to nut margarines with a considerable content of acids of low molecular weight. It is caused by hydrolysis of the fat through the action of lipolytic enzymes developed from bacterial contamination. Free fatty acids of 16 to 18 carbon atoms are not sufficiently soluble to have a noticeable taste, but the acids of low molecular weight of coconut oil are quite objectionable in concentrations of 2–3% or more.

Margarines which contain as much as 3% of salt and are stored under refrigeration are unlikely to spoil through bacterial action, even in the absence of sodium benzoate or other preservative. Margarine which is to be held without refrigeration should contain a preservative.

Considerable care must be exercised, particularly in the packaging operation, to avoid contaminating the product with molds, many of which will grow freely on the surface of even strongly salted margarine. It is possible to buy wrappers which are, for all practical purposes, sterile; but they may be easily contaminated by careless handling. The best margarine plants are air conditioned, with filtered air, to guard against the possibility of air-borne mold contamination.

Under ordinary conditions of handling and storage, margarine undergoes no significant reduction in vitamin A content. However it may suffer

[41c] L. Peters, U. S. Pat. 2,347,640 (1944).
[41d] J. E. Slaughter, Jr., and C. E. McMichael, *J. Am. Oil Chem. Soc.*, *26*, 623–628 (1949).

a substantial loss over extended periods, *e.g.*, 35% in samples stored for a year at 10°F.[42]

Kiess *et al.*[43] have reported that they were able to store margarine of different types at −10° or 5°F. for 538 days without flavor deterioration, but that deterioration was relatively rapid at 28° or 45°F.

[42] E. B. Boyce, L. E. Filos, and H. C. Lythgoe, *Quarterly Bulletin of the Association of Food and Drug Officials of the United States*, *10*. No. 3, 97–104 (1946).

[43] A. A. Kiess. R. W. Bates, and C. K. Wiesman, *Food Inds.*, *20*, 716–718, 825 (1948).

BAKERY PRODUCTS AND CONFECTIONS

A. Introduction

A large part of the total production of lard, shortening, and certain other plastic fats is consumed in the manufacture of commercial baked goods. The average percentages of fat in some of the more popular bakery products are approximately as follows: pie crust, 35–50; pound cake, 15–30; doughnuts, 15–20; cookies and wafers, 5–20; white and yellow layer cakes, 12 to 15; soda crackers, 8 to 12; pretzels, 5; and white bread, 3.

In 1947 the total consumption of fat products in commercial baked goods in the United States was 791,707 thousand pounds (Table 80). In point of dollar value, the fats comprised 21.4% of the total raw materials used. The total value of the finished baked products amounted (Table 79) to over 2.5 billion dollars.

In most classes of baked goods, fat is a highly necessary ingredient, not only because of its contribution to the flavor of the product, but also because it plays an essential role in the development of the physical structure. Such important considerations as the volume, the texture, and the tenderness of the finished goods are all closely related to the amount of fat used in the formula, the methods employed in incorporating it, and the inherent characteristics of the fat itself.

There are considerable differences in the manner in which different kinds of fat behave in the manufacture of specific classes of baked goods. In some cases these differences are not extreme, and may in fact be so slight as to pass unnoticed in ordinary household use of the fats. In the highly competitive business of commercial baking, however, even minor differences may lead to pronounced discrimination between different fats, with the establishment of corresponding differentials in the prices prevailing for the fats.

It is highly desirable for baking fats to be uniform in quality, as an occasional batch of inferior goods may damage a baker's reputation out of all proportion to the actual amount of merchandise involved. Consequently, manufacturers of the better grades of fat products exert every effort to produce materials which are invariable in all important characteristics.

TABLE 79

PRODUCTION OF BAKED GOODS IN COMMERCIAL BAKERIES IN UNITED STATES IN 1947[a]

Item	Production, 1000 lbs.	Value, 1000 dollars
White pan bread	8,521,157	937,560
White hearth bread	306,117	37,882
Whole wheat and other dark wheat breads	893,411	105,487
Rye and pumpernickel bread	613,391	78,016
Raisin and specialty breads	192,476	27,813
Breads, classification not reported	—	10,098
Rolls, bread type	942,791	152,643
Sweet yeast-raised goods	612,328	182,169
Doughnuts, cake type	309,591 (doz.)	80,203
Soft cakes	1,210,207	390,663
Pies	600,641	146,750
Pastries, all types	—	20,792
Cookies, hand made	80,596	25,115
Rolls, cakes, etc., classification not reported	—	13,066
Cookies, machine-made	1,027,216	327,102
Crackers, all types	983,790	213,326
Pretzels	74,168	17,377

[a] U. S. Bureau of the Census, *Census of Manufactures*, 1947.

TABLE 80

PRINCIPAL MATERIALS CONSUMED IN MANUFACTURE OF BAKED GOODS IN COMMERCIAL BAKERIES IN UNITED STATES IN 1947[a]

Material	Biscuit and cracker factories only		All bakeries	
	Quantity, 1000 lbs.	Value, 1000 dollars	Quantity, 1000 lbs.	Value, 1000 dollars
Wheat flour	1,428,800	74,865	9,702,300	570,383
Sugar	238,521	20,820	1,139,096	97,904
Lard	103,107	27,541	350,597	93,032
Shortening	55,398	16,571	315,872	99,778
Other fats and oils	70,943	18,790	125,238	37,700
Dried milk	8,893	1,581	223,929	29,558
Frozen eggs	9,139	3,104	196,702	66,169
Dried eggs	288	347	926	1,125

[a] U. S. Bureau of the Census, *Census of Manufactures*, 1947.

B. Structural Considerations

1. STRUCTURE OF BAKED PRODUCTS

If bread, cake, pastries, etc., are examined closely, it will be seen that they are more or less cellular in form, and contain a large proportion of

voids. The adequate development of this cellular structure leads to the lightness and tenderness which is generally associated with good baked products. The importance of good structure is particularly evident in the manufacture of cakes. The difference between light, well-formed cakes and those which are complete failures usually lies solely in the relative proportions of solid materials and voids in the two.

Good volume in breads, cakes, and similar products is considered particularly essential by the commercial baker. This is true not only because good volume is associated with good texture and other desirable properties, but also because the purchaser is inclined to judge the baker's offerings by their apparent size rather than by their weight.

The size of the individual cells is also a matter of some importance, as fine- and even-grained products are superior in appearance and texture to those which are coarse and irregular in grain. Thus the volume of baked products cannot well be developed at the expense of grain and texture. The fineness or coarseness of grain depends upon the average size of the cells. The evenness of grain depends upon their size distribution.

The cellular structure of baked products is produced by the expansion of gases within the dough while the latter is still soft and extensible. In the following pages, the term "leavening" is applied generally to the process of gas generation and expansion, with accompanying increase in volume of the product.

From the standpoint of the leavening process, baked goods may be divided into two broad classes, namely, those which are leavened with yeast and those which are leavened by other means. In the case of yeast-raised goods, leavening occurs over a considerable period of time, and is partially effected before the dough enters the oven. In most doughs which are leavened without the use of yeast, leavening is much more rapid, and occurs principally after the dough is subjected to the heat of the oven.

In bread and other yeast-leavened products, a fairly satisfactory cellular structure may be produced without fat being present. There are also a few non-yeast-raised products, such as sponge cakes, in which fat does not play an essential role in the leavening process. Other types of cakes, however, and many other products, require a considerable proportion of fat for the development of their characteristic structure.

A second important function of the fats used in baking is one of lubrication. If a finished baked product of the cake type is subjected to microscopic examination, it will be seen that the solid material comprising it is not homogeneous. The continuity of the gluten and starch structure comprising the cell walls is broken by films of fat. These weaken the structure of the product sufficiently to make it tender and easily disintegrated when it is eaten.

Certain baked products, such as pie crust and certain pastries and cookies, are formed from a stiff dough rolled into a thin sheet. The rolling process has the effect of spreading the incorporated fat into thin, parallel layers. In the finished products, the natural lines of cleavage are along the fat layers; thus a "flaky" structure is produced. All cookies, biscuits, wafers, etc., which are baked in a thin form from a dough low in moisture, require a large percentage of fat, to prevent the relatively dry gluten and starch from compacting into a hard, refractory mass.

2. Relation of Fat to Leavening Process

Although fat plays an important role in the leavening of other products, its peculiar action is best exemplified in the manufacture of ordinary yellow cakes. Cake doughs consist of certain dry, or nonaqueous, ingredients —flour, sugar, salt, baking powder, fat etc.—mixed with other watery or liquid ingredients—egg and milk. In the process of mixing, the sugar, baking powder, and salt dissolve in the liquid ingredients.

The resulting solution mixes freely with the particles of flour, but not with the fat. Thus the dough is in effect a two-phase system. The two phases consist, respectively, of the fat, and all the other ingredients of the mixture.

If a small amount of an oil-soluble dye is added during the mixing operation, to stain the fat, and the dough is examined under the microscope, the fat will be seen to be dispersed throughout the dough in the form of small, irregularly shaped particles (Fig. 37). Within each particle of fat there will be enclosed numerous small bubbles of air, incorporated during the mixing operation. No air will be entrapped in the aqueous phase of the dough.

The examination of numerous different samples of dough will reveal that there is usually some variation with respect to the size of the fat particles and the amount of incorporated air. If the doughs are baked into test cakes, it will be found that there is a close correlation between the volume and other qualities of the finished cakes, and the structure of the doughs from which they are baked. The doughs containing large amounts of air entrapped within the fat will produce cakes larger in volume than will those containing relatively little air (Figs. 38, 39). And cakes made from doughs in which the entrapped air is well dispersed will have a finer grain and texture than those in which it is not well distributed. They will also be less inclined to fall or collapse while they are being baked.

The ingenious experiments of Carlin,[1] involving the actual baking of cake batters under the microscope, have revealed the reason for the cor-

[1] G. T. Carlin, *Cereal Chem.*, *21*, 189–199 (1944).

a   b
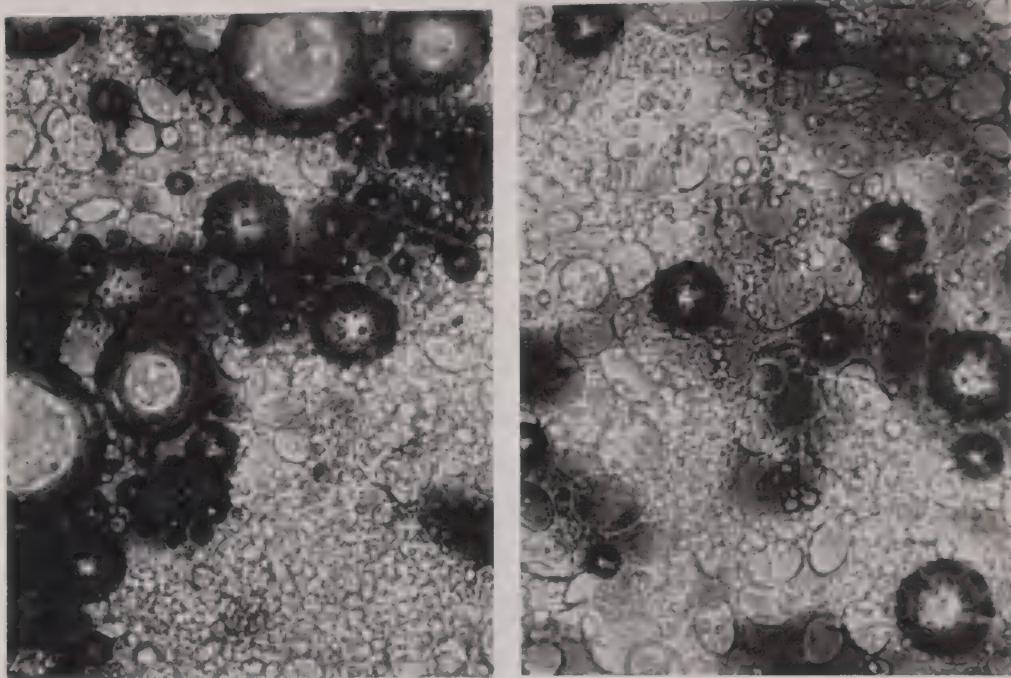
Fig. 37. Photomicrographs ($\times$290) of pound cake doughs with: (a) good incorporation of air and (b) poor incorporation of air.

a   b
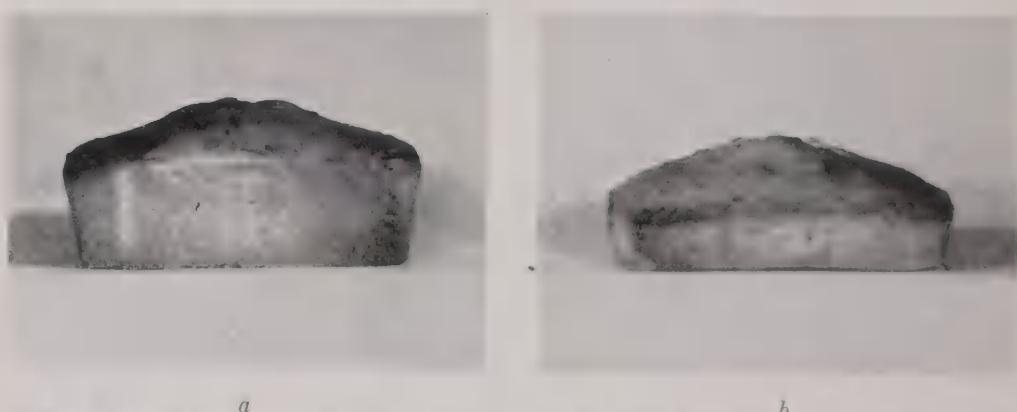
Fig. 38. Cakes from pound cake doughs with: (a) good air incorporation, and (b) poor air incorporation (cf. Fig. 37).

relation between fat dispersion and fineness of grain, and air incorporation and cake volume. The fat particles in the batter comprise the points at which pockets of leavening gases form, and hence the points at which open cells appear in the baked product. As the fat melts, from the heat of the oven, the entrapped air migrates to the water–fat interface, and

there serves as a nucleus for the accumulation of water vapor and carbon dioxide produced from baking powder or other chemical leavening agent, gas cells do not appear spontaneously. Naturally, as the gases expand further, cleavage of the dough mass takes place most readily along the fat boundaries.
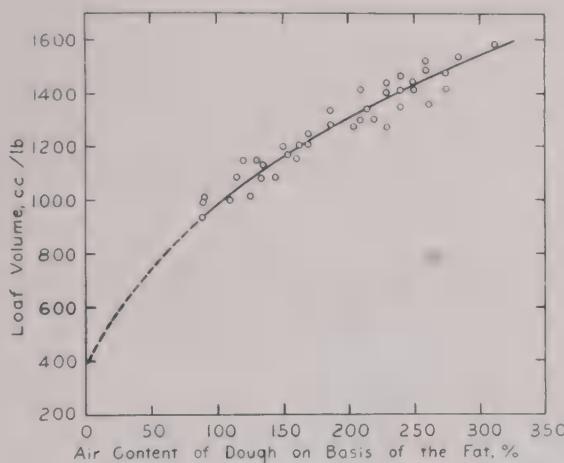
Fig. 39. Air content of pound cake doughs (without chemical leavening agent) *vs.* loaf volume of the finished cake.

Because it serves to initiate gas expansion, the air in the fat contributes a leavening action out of proportion to its normal thermal expansion in the oven. The experiments in Table 81 illustrate the typical effect of the incorporation of air in a pound cake formula containing 21% fat and no chemical leavening agent. To these may be added the observation by Dunn and White[2] that pound cake doughs wholly devoid of air do not rise at

TABLE 81

TYPICAL EFFECT OF INCORPORATING AIR IN POUND CAKE FORMULA CONTAINING
21 PER CENT FAT AND NO CHEMICAL LEAVENING AGENT

Experiment	A	B
Air incorporation in shortening..................................	Low	High
Calculated volume of dough without air, cc......................	377	377
Actual volume of dough, including air incorporated, cc...........	543	662
Volume of air in dough, cc......................................	166	285
Volume of cake, cc...	1140	1520
Expansion of dough during baking, cc...........................	597	858
Calculated expansion of air due to heating in oven (70–212°F.), cc.....	42	71
Percentage of total expansion due to thermal expansion of air......	7.0	8.3
Percentage of total expansion due to increased vapor pressure of water	93.0	91.7

[2] J. A. Dunn and J. R. White, *Cereal Chem., 16,* 93–100 (1939).

all when baked. It is apparent that the thermal expansion of the air is a very minor factor in the leavening process, and that the greater part of the expansion of the dough in the oven is due to the increased vapor pressure of water in the air bubbles at high temperatures. Water vapor can not assist in the leavening process unless air is initially present in the dough, and the extent to which it assists is more or less proportional to the amount of air present.

An important feature of the leavening contributed by water vapor in conjunction with air is that it is controlled, *i.e.*, the expansion of gas takes place at points which are predetermined by the position of the fat-entrapped air bubbles. By conducting the mixing operations in such a manner as to cause the fat to enclose much air, and then distributing the fat well through the dough, leavening can be made to take place uniformly through the dough, with the production of a cake of fine and uniform grain and texture.

In actual practice, most cakes are made with an insufficient quantity of fat to supply the entire amount of leavening desired, hence the action of the air and water vapor must be supplemented by carbon dioxide generated from baking powder or other suitable chemical leavening agent. If the leavening supplied by the baking powder is not disproportionate to that obtained from the air and water vapor, a cake of good structure results, as in this case the carbon dioxide appears merely to reinforce the action of the water vapor. If too little air is incorporated in the fat, however, and the deficiency in air is compensated by the use of an excessive amount of baking powder, the cake will be coarse grained, with many large cavities and tunnels, from the action of the baking powder being uncontrolled by the air.

In the manufacture of pound cakes without the use of baking powder no particularly good dispersion of the fat is obtained (compare, for example, Figures 37 and 45), but a very fine-grained cake is obtained, due to the fact that the leavening action is entirely controlled by the incorporated air.

A fine cellular structure is also desirable in cake making because of the mechanical strength which it imparts to the dough. The sugar used in cake and other sweet doughs weakens the dough and tends to make it more fluid than unsweetened dough. Consequently, cake doughs are particularly prone to fall or collapse of their own weight during that period of the baking operation just prior to their assuming a "set" form, due to coagulation of the starch and protein in the flour.

A soft, partially baked dough of fine cellular structure is much stronger and less likely to collapse than one of coarse structure.

3. Shortening Values of Different Fats

The ability of a fat to lubricate and weaken the structure of a baked product is known as its shortening value. The relative shortening values of different fats may be determined by means of the "shortometer." This instrument, which was devised by Davis[3] and improved by Bailey[4] measures the breaking strength of standard test biscuits or wafers, which are shortened with the fats under test.

Somewhat discordant results have been obtained by the various investigators who have attempted to evaluate different fats on the basis of their shortening power.[5] However, it would appear that the shortening value
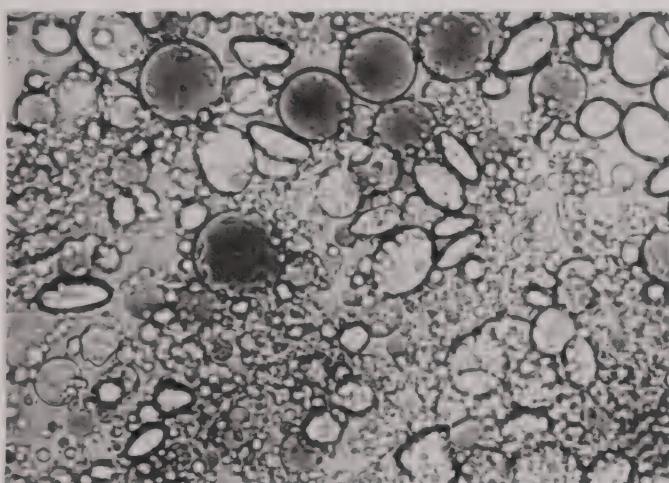
Fig. 40.   Photomicrograph (×300) of pound cake dough made with a liquid oil.

of a fat is principally dependent upon its consistency, soft fats, such as prime steam lard, being superior in this respect to firmer fats, such as all-hydrogenated shortenings. The superior shortening value commonly attributed to lard may also be related to the characteristically coarse crystal structure of this fat.

Platt and Fleming[6] reasoning from the concepts of surface chemistry developed by Harkins, Langmuir, and others, have advanced the theory that the particular effectiveness of lard as a shortening material is related to its relatively high content of unsaturated fatty acids. This theory, however, does not appear to be supported by experimental evidence.

[3] C. E. Davis, *Ind. Eng. Chem., 13,* 797–799 (1921).
[4] C. H. Bailey, *Cereal Chem., 11,* 160–163 (1934).
[5] See, for example, J. D. Fisher, *Ind. Eng. Chem., 25,* 1171–1173 (1933); A. W. Harvey, *ibid., 29,* 1155–1159 (1937); and L. R. Hornstein, F. B. King, and F. Benedict, *Food Research, 8,* 1–12 (1943).
[6] W. Platt and R. S. Fleming, *Ind. Eng. Chem., 15,* 390–394 (1923).

The inadequacy of liquid oils as shortening agents is undoubtedly due to their lack of plasticity. Particles of oil in a dough are drawn into spherical globules by their surface tension (Fig. 40), and thus cannot be dispersed in streaks and films through the dough in the manner of plastic fats.

4. CREAMING QUALITY

The absorption of air by fats during mixing operations in the bakery is termed "creaming." As explained above, the creaming ability of a fat is a highly important factor in determining its value as a shortening agent.

The creaming quality of a fat may be tested, or the creaming may be followed through the various stages of preparing a dough, by periodically
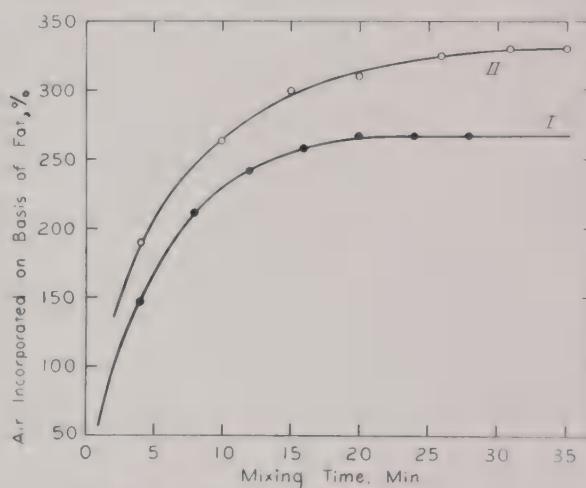
Fig. 41. Typical creaming tests of a shortening with good creaming properties: (I) 40% fat, 60% sugar, by weight, (II) 30% fat, 33% sugar, 37% eggs.

determining the density of the dough or other mixture. The creaming is best expressed as the percentage of air incorporated by the fat, on the basis of its own volume.[7] When a test is conducted by simply mixing together fat and sugar, the relative proportions of fat and sugar and the size and shape of the sugar granules influence the amount of air which the fat will absorb. The optimum ratio of sugar to fat for maximum air incorporation is approximately 3 to 2, by weight. The finer the granulation of the sugar, the greater is the incorporation of air.[8] Decreasing the particle size by grinding is not effective in promoting increased creaming, however, as the ground particles are less effective in entrapping air than are naturally formed crystals. The action of sugar in promoting air ab-

[7] See A. E. Bailey and R. H. McKinney, *Oil & Soap*, *18*, 120–122 (1941).
[8] J. A. Dunn and J. R. White, *Cereal Chem.*, *14*, 783–801 (1937).

sorption appears to be purely mechanical. The presence of any other granular substance will also increase the capacity of fats to take up air.

Different fats may differ markedly in their creaming properties. Typical creaming tests on different fats at 70°F. with a 3 to 2 ratio of sugar to fat are shown in Table 82 (see also Fig. 41). For fats to cream satisfactorily it appears to be necessary for them to contain certain highly saturated glycerides.[9] Hydrogenation appears to be particularly effective for the production of good creaming fats. Limited hydrogenation of any oil or soft fat will produce a shortening of good creaming quality, as will the addition of a small proportion of highly hydrogenated fat. Lard will not cream well without hydrogenation or the addition of hydrogenated

TABLE 82

CREAMING TESTS OF VARIOUS FATS AT 70°F.[a] (AIR INCORPORATION CALCULATED BY VOLUME, ON THE BASIS OF THE FAT)

Fat	Iodine value	Per cent air incorporated after mixing for specified times, (min.)						
		4	8	12	16	20	24	28
All-hydrogenated vegetable shortening..	62	165	215	240	265	275	280	280
Compound-type shortening "A"[b]	90	190	240	270	280	280	280	280
Compound-type shortening "B"[c]	73	150	195	230	255	270	275	275
Prime steam lard.	69	85	125	145	150	155	155	155
Prime steam lard with 8% hydrogenated lard stearine added.	65	155	205	235	260	270	275	275
Hydrogenated prime steam lard.	61	150	200	240	260	270	275	280
All-hydrogenated vegetable shortening, untempered.	62	120	160	175	180	185	185	185

[a] 1.0 lb. fat mixed with 1.5 lbs. fine granulated fruit sugar at medium speed in Hobart bench mixer with 12-qt. bowl.

[b] Compounded from slightly hydrogenated cottonseed oil and hydrogenated cottonseed oil stearine.

[c] Compounded from vegetable stearine, slightly hydrogenated cottonseed oil, and tallow.

fat. The creaming quality of butter is variable and generally inferior to that of hydrogenated or compounded shortenings. "Untempered" shortenings, *i.e.*, shortenings placed directly under refrigeration after filling, without a tempering period at about 85°F., are notably deficient in creaming quality.

When cakes are mixed by the common "sugar batter" method, wherein the shortening is mixed first with the sugar, then with the eggs, and last of all with the milk and flour, the fat is not ordinarily creamed to its maximum air content in the first stage of mixing. The usual practice is first to cream the shortening and sugar to an air content of 150–200% on the basis of the fat, and then add the eggs. The presence of the eggs increases

[9] Glycerides of intermediate melting point separated from hydrogenated lard or all-hydrogenated shortenings cream very poorly, even though they have the consistency of shortening at the temperature at which the creaming tests are conducted.

the capacity of the shortening to hold air; after their addition to the mix, the air content of the fat may usually be increased to 275–325%.

Hydrogenated lard or lard with hydrogenated "flakes" added incorporates air well when creamed with sugar, but has the peculiarity of tending to lose rather than gain air when eggs are mixed into the fat–sugar mass. This loss of air, accompanied by partial breaking of the fat–egg emulsion, appears to be associated with the characteristic coarse crystal structure of lard products (see Fig. 15, Chap. VIII), inasmuch as a similar effect occurs with vegetable shortenings if the latter are melted and then slowly solidified, to produce large crystals. It can be prevented by applying heat to the mixture, to prevent a drop in temperature as the sugar dissolves, and it does not occur when the cake is mixed by the "flour batter" method (page 319), i.e., when the sugar is dissolved in the eggs before they are mixed with the fat. Because of this peculiarity of lard shortenings, the latter method or some modification is usually followed when they are used in cake making.

The maximum amount of air which a fat is capable of incorporating does not vary a great deal over a considerable temperature range, although within their effective creaming range, fats will cream more rapidly when soft than when relatively firm. Manufacturers naturally endeavor to produce shortenings which have optimum properties at ordinary mixing temperatures. The recommended working range for all-hydrogenated shortenings is 70° to 80°F., although most products will mix and cream satisfactorily at temperatures 10° outside of this range on either the high or the low side. Compound-type shortenings will cream well over a wider temperature range than all-hydrogenated products.

5. EMULSIFICATION AND DISPERSION

As stated previously, a cake dough is actually an emulsion, in which the internal phase is the fat and the external phase is comprised of the remaining ingredients. Since the fat is plastic, rather than liquid, the oily phase consists of irregularly shaped particles, rather than spherical globules. Thus the fat particles cannot actually coalesce, as in an ordinary oil-in-water emulsion. However, they may agglomerate into large masses, and in general the problems involved in producing a good emulsion in a dough are analogous to those encountered in producing emulsions of liquid oil in an aqueous medium.

One of the functions of the eggs used in cakes is to serve as an emulsifying agent, to promote dispersion of the fat. However, shortenings are available which contain more powerful synthetic emulsifying agents. These so-called "superglycerinated" shortenings (see pages 255–257), contain mono- and diglycerides which are extremely effective in promot-

ing and stabilizing emulsions of both the water-in-oil and oil-in-water types. More recently, it has been found that the partial fatty acid esters of sorbitol[10] and their polyoxyethylene derivatives[11] are also good emulsifying agents, and there is now a considerable use of these materials in commercial bakeries. Up to the present, however, these have been marketed separately, and used in conjunction with an ordinary shortening, rather than as a shortening ingredient. According to the patent literature,[11] the partial sorbitol esters can be made relatively fat-soluble or relatively water-soluble, according to the relative proportions of fatty acids and ethylene oxide used in making up the molecule; e.g., sorbitan monostearate is relatively soluble in fat if condensed with 4 moles of ethylene oxide, but relatively soluble in water if it is condensed with 20 moles of ethylene oxide. The best results in baking are said to be obtained if the emulsifier is partially water-soluble. Mono- and diglycerides, it is to be noted, are soluble only in fat.

While the effectiveness of the aforementioned materials in cake doughs is explainable in terms of conventional theories of emulsification, on the basis of their content of hydrophilic (hydroxyl) and lipophilic (fatty acid) groups, it is nevertheless somewhat surprising that they are so much more efficient than a number of other emulsifying agents. There are other edible emulsifiers, such as soybean lecithin, which are very effective in lowering the interfacial tension of fat against water, but none of these is capable of conferring satisfactory emulsifying properties upon baking fats.

The principles involved in the use of superglycerinated shortenings have been discussed at some length in a preceding chapter. As mentioned previously, the difficulty of maintaining the fat in sweet dough in a highly dispersed condition increases with increasing water and sugar content of the dough. With ordinary fats it is not possible to produce a good cake dough if the combined amount of milk and sugar in the formula amounts to more than about 40 to 45% of the total ingredients. With the use of added emulsifying agents it is possible to increase the milk and sugar to as much as 50 to 55% of the total. The difference between ordinary fats and superglycerinated fats, with respect to their dispersion in high sugar and liquid content doughs, is shown in the photomicrographs of Figure 42.

Many vegetable shortenings put up for household use, and at least one popular animal fat shortening are superglycerinated to improve their cake-making properties, and particularly to permit them to be used in cakes made by the so-called "quick-mix" method.

Since shortening, lard, and similar fats are plastic products, with a more or less rigid structure, they are capable of absorbing and holding consider-

[10] K. R. Brown (to Atlas Powder Co.), U. S. Pats. 2,303,432 (1942); 2,322,820–822 (1943).

[11] N. F. Johnston (to R. T. Vanderbilt Co.), U. S. Pat. 2,422,486 (1947).

able quantities of water without benefit of an emulsifying agent. The extent to which a fat is capable of taking up water may be determined by slowly mixing water into the fat in a small baker's mixing machine. For some reason, hydrogenation improves the ability of a fat to emulsify water. Lard and compound-type shortenings consisting principally of unhydrogenated oil will usually absorb 25 to 50% of water at 70°F., whereas hydrogenated lard will absorb 75 to 100% and all-hydrogenated vegetable shortenings will take up 150 to 200%. Shortenings containing mono- and diglycerides will emulsify 400% or more of their own weight of water, assuming in the process an elastic, gel-like structure.
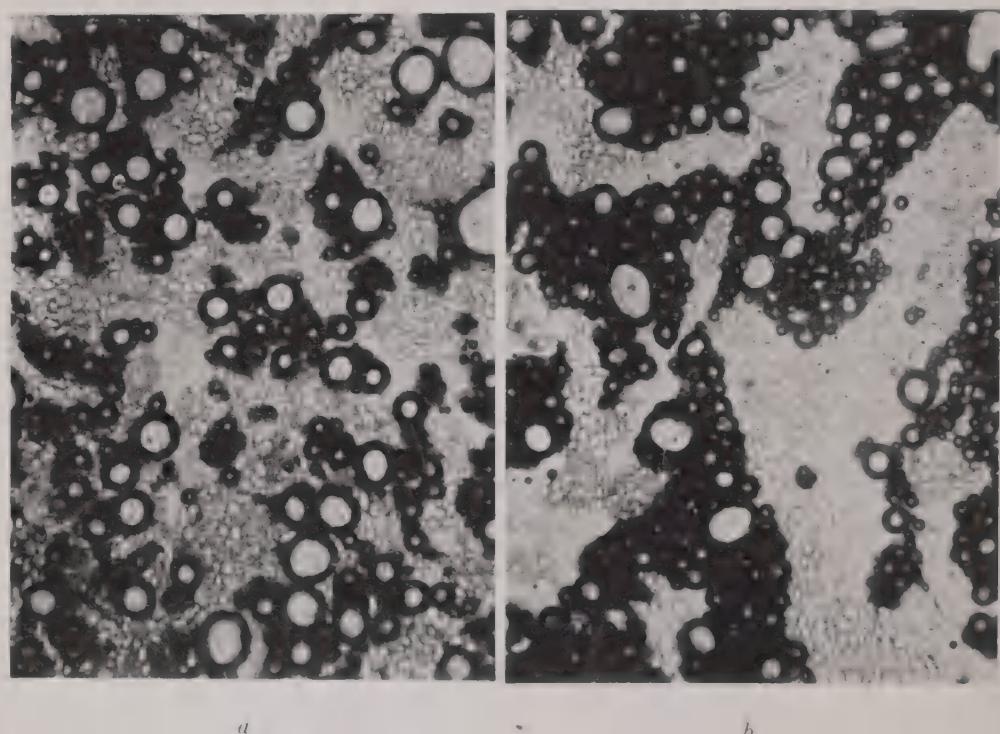
Fig. 42. Photomicrographs (×72) of high-sugar yellow cake doughs made with: (a) superglycerinated shortening, and (b) ordinary shortening.

From a practical standpoint, the variations in water-absorbing capacities of different fats do not appear to be as significant as might be supposed. When compound-type shortenings of low emulsifying capacity and nonsuperglycerinated all-hydrogenated shortenings of high emulsifying capacity are mixed with eggs, in the actual manufacture of cake or other sweet doughs, there is no apparent difference in either the water-in-oil emulsions of sugar, fat, and eggs, or the oil-in-water emulsions of the finished doughs. However, the ability to absorb water is important in the manufacture of icings, etc.

C. Nonstructural Considerations

1. Stability of Fats in Baked Goods

A large volume of baked goods consists of products such as soda crackers and various sweet biscuits, which are normally packaged and held for a considerable time before they are consumed. As these products are not commonly packed in containers which protect the contents from the air, the fat used in their manufacture may in time become rancid.

The matter of fat stability in baked goods has not been extensively investigated. However, the investigations which have been reported have emphasized that the problem is considerably different from that of the stability of fats in their original form. The difference observed between the deterioration of pure fats and the same fats in baked goods is probably associated with both the heat treatment accorded the fat in the baking process and the presence of materials in the flour and other ingredients of the mixture, which influence the oxidation of the fat.

Various investigators have observed a lack of correlation between the keeping qualities of different fats and the stability of crackers and other products made from the same fats. Triebold, Webb, and Rudy[12] found that in some cases lards which were on the verge of rancidity produced crackers of better keeping quality than did lards of good stability. Bohn and Olson[13] prepared soda crackers from different fats, and observed that the stability of the crackers decreased, not with the stability of the fats, but with increase in the degree of unsaturation of the fats. They attributed this effect to the destruction of antioxidants in baking, which would of course make the stability of the fat entirely dependent upon its fatty acid composition. They found that commercial crackers made with corn oil became rancid almost immediately at 145°F., but that crackers made with lard would withstand accelerated oxidation at this temperature for 2 to 6 days. They also found that crackers made with oleo oil would keep under the same conditions for 6 to 15 days, and that crackers made with all-hydrogenated vegetable shortenings of the biscuit and cracker type would keep as long as 40 days. The stabilities of corn oil, lard, oleo oil, and all-hydrogenated shortenings of this type, as measured by the Swift accelerated method, were of the order of 10, 8, 12, and 120 hours, respectively.

The conclusions of Bohn and Olson were confirmed in some respects by McKinney and Bailey,[14] who found biscuits made with hydrogenated lard to be virtually as stable as those prepared from hydrogenated vegetable

[12] H. O. Triebold, R. E. Webb, and W. J. Rudy. *Cereal Chem.*, *10*, 263–276 (1933).
[13] R. M. Bohn and R. S. Olson. *Oil & Soap*, *11*, 210, 218 (1934).
[14] R. H. McKinney and A. E. Bailey, *Oil & Soap*, *18*, 147–148 (1941).
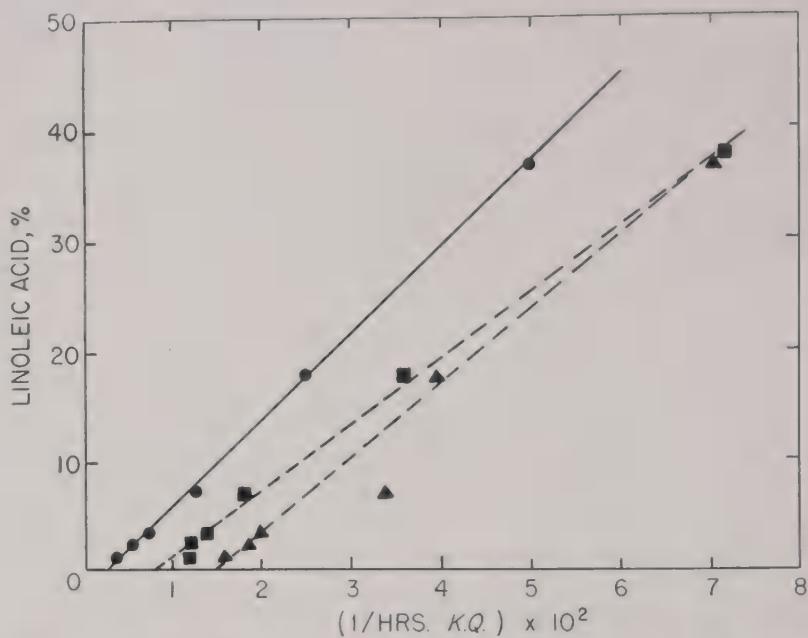
Fig. 43. Linoleic acid content of hydrogenated cottonseed oil shortenings *vs.* reciprocal of the keeping time of the shortenings and of ration biscuits made therefrom. (Circles represent shortenings alone, triangles represent Type I biscuits, squares represent Type IV biscuits.) From data of Horne *et al.*[16]
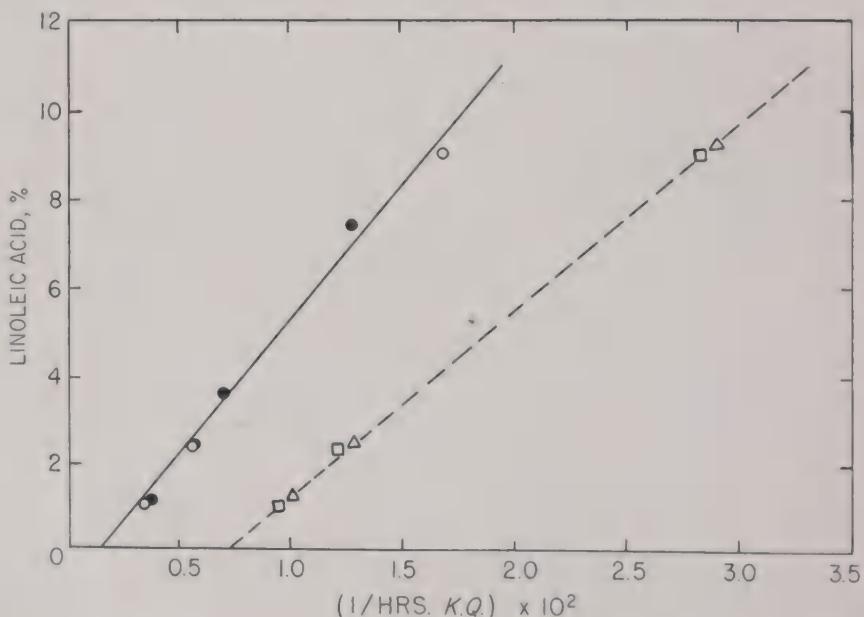
Fig. 44. Linoleic acid content (including linolenic acid in term of linoleic) of hydrogenated soybean oil shortenings *vs.* reciprocal of the keeping time of the shortenings and of biscuits made therefrom. (Open circles represent shortenings alone, triangles represent Type I biscuits, squares represent Type IV biscuits. For comparison, closed circles show the corresponding relationship for hydrogenated cottonseed oil shortenings.) From data of Horne *et al.*[16]

oil shortenings. That lard is very low in its content of natural antioxidants, in comparison with vegetable oils, is well known.

The suggestion of Triebold et al.[12] that the stability of a lard may be unimportant in its bearing on the stability of crackers made therefrom has been disputed by Maveety,[15] who has given the following average results of a number of tests:

Keeping time of lard, hours, A.O.M.	Keeping time of crackers, days at 125°F.
1 to 3	30
3 to 4	43
4 to 5	53
5 to 6	40
6 to 7	48
7 to 8	61
8 and above	63

Since the crackers kept about four times as long at ordinary winter room temperatures (about 70°F.) as at 125°F., those made with 1–3 hour lard could be expected to have a shelf life of not more than 4 months, as compared with about 8 months for those made with lard having a stability of 7 hours or more. However, it will be noted that these results indicate relatively little difference in lards varying in keeping time within the range of about 4–8 hours.

Recently, Horne and co-workers[16] have published the results of an extensive series of tests in which lard, and also a series of cottonseed and soybean oils hydrogenated to different degrees, were incorporated (in a commercial bakery) into army ration biscuits, which were then subjected to accelerated stability tests at 216°F. in the "rancimeter" apparatus[17] commonly used for cereal products. It has been pointed out in a previous chapter (page 251) that the oxidative characteristics of unsaturated fatty acids lead to a linear relationship between the reciprocal of the keeping time of a fat and the concentration of active methylene groups, as determined by the content of linoleic and linolenic acids. In the case of the experiments of Horne et al. it appears that this relationship was valid not only for the pure fats, but also for the two types of biscuits tested (Figs. 43 and 44), although in the case of the latter, the difficulty of eliminating uncontrolled variables from the tests naturally led to a somewhat wider scattering of experimentally determined points. No great differences were noted between the cottonseed and the soybean oil samples, either as such, or after incorporation into the biscuits, but the lard biscuits were less stable than biscuits made with vegetable fat of equivalent composition, which may indicate that the natural antioxidants of the latter were not completely inactivated by baking.

[15] D. J. Maveety, Oil & Soap, 23, 25–27 (1946).
[16] L. W. Horne, H. H. Stevens, and J. B. Thompson, J. Am. Oil Chem. Soc., 25, 314–318 (1948).
[17] F. E. James, Food Inds., 17, 492–493 (1945).

Subsequent storage tests at 70° and 100°F.[18] revealed a reasonably good correlation between the accelerated stability and the actual storage life of the biscuits, with one hour at 216°F. being equivalent to about one month at 70°F. and about 0.3 month at 100°F. For the biscuits to be sure of keeping for 12 months at a maximum temperature of 100°F. it was concluded that it was necessary to specify a vegetable oil shortening with a minimum A.O.M. stability of 100 hours, corresponding to a linoleic acid content (determined spectrophotometrically) of about 5.3%.

The Type I and Type IV biscuits used for the test contained 10.0% and 14.3% fat in the formula, respectively, and 3–4% sugar. The Type IV formula for the cottonseed oil and lard biscuits contained 2% lecithin, on the basis of the fat.

Grant and co-workers[19] found that nonsweetened army ration biscuits did not remain in good condition for longer than 22 weeks at 110 F. even when made with shortening of very high stability (over 200 hours, A.O.M.). As the peroxide value of the extracted fat was low at the end of this time, the failure of the biscuits to keep longer was attributed to the deterioration of ingredients other than fat.

The development of rancid odors in packaged biscuits and similar products can often be traced to advanced oxidation, not in the packaged product, but in a film of fat which has been transferred to the inner wrapper. Hence this wrapper should be nonabsorbent, and should not contain substances which catalyze oxidation. Patents have been taken out for antioxidant compositions to be applied to wrapping papers.[20] Vacuum packing is effective for extending the keeping time of special products.[15]

Most of the workers who have investigated the effect of lecithin in baked goods have failed to find that it has any marked effect on the stability of the latter,[13,14,16] even though it may have a beneficial effect on the shortening material alone. Maveety[15] has reported that 0.15% 0.15% lecithin added to lard may increase the keeping quality of crackers from 25 to 180%. The antioxidants added commercially to lard vary greatly in the degree to which their effectiveness carries over into baked products. Gum guaiac[21] and butylated hydroxyanisole[22] have been reported to be virtually as effective in baked goods as in pure fats. NDGA

[18] H. H. Stevens and J. B. Thompson, *J. Am. Oil Chem. Soc.*, 25, 389–394 (1948).
[19] G. A. Grant, J. B. Marshall, and W. H. White, *Can. J. Research*, F23, 123–131 (1945).
[20] See, for example, H. S. Mitchell (to Industrial Patents Corp.), U. S. Pats. 2,155,731 (1939), 2,309,079 (1943), and 2,344,470 (1944); S. Musher (to Musher Foundation, Inc.), U. S. Pats. 2,324,529 and 2,325,624 (1943).
[21] J. W. Higgins and H. C. Black, *Oil & Soap*, 21, 277–279 (1944).
[22] H. R. Kraybill, L. R. Dugan, Jr., B. W. Beadle, F. C. Vibrans, V. Swartz, and H. Rezabek, *J. Am. Oil Chem. Soc.*, 26, 449–453 (1949).

(nordihydroguaiaretic acid) appears to carry over to some extent,[21,23] but propyl gallate and tocopherols are quite poor in this respect.[21] The carry-over, particularly of acidic antioxidants, is better in a simple product like pie crust than in an alkaline product such as soda crackers. Compounds of high water solubility invariably have a poor carry-over.[24]

Sweet biscuits or cookies are naturally much more stable than soda crackers or other unsweetened products. Sugar itself acts as a powerful antioxidant,[13,14] as do also molasses, [15] certain spices,[15] and, to some degree, chocolate or cocoa.[25]

Soda crackers, according to Bohn and Olson,[13] are extraordinarily susceptible to metallic contamination, and are considerably injured in keeping quality by being mixed in commercial steel equipment. Crackers mixed in glass in the laboratory and subjected to accelerated oxidation at 145°F. were found to be markedly superior in keeping quality to crackers containing the same fats, but mixed in the factory. In some cases, even the use of a metal cutter on cracker doughs otherwise unexposed to metal surfaces decreased the stability of the crackers by as much as 50%. This seems remarkable in view of the fact that flour and other cracker ingredients commonly contain several parts per million of both iron and copper. The heavy metal content of lard or shortening is usually of the order of a small fraction of one part per million.

In some cases, baking probably develops rather than destroys antioxidants, e.g., the heat treatment of milk, if milk is an ingredient, is known to produce sulfhydryl antioxidants from milk proteins.

2. Behavior of Fats in Commercial Deep Frying

Large quantities of oils and fats are used in the commercial frying of such products as doughnuts, potato chips, nuts, etc., as well as in the preparation of a variety of fried foods in restaurants and hotels.

Commercial frying differs from that practiced in the household in that the products to be cooked are invariably "deep-fried," by immersion in a large body of fat, rather than being merely sautéed. Also, the large quantities of material passed through the fat make a constant replenishment of it necessary. Consequently, the contents of the frying kettle consist of a mixture of comparatively fresh fat with fat which has undergone an indefinite period of use.

For products which are fried in large quantities, such as doughnuts, the frying kettles are usually equipped with thermostatic controls, which maintain the fat at a constant temperature, and with fully automatic

[23] W. O. Lundberg, W. O. Halvorson, and G. O. Burr, *Oil & Soap, 21*, 33–35 (1944).

[24] K. F. Mattil and H. C. Black, *J. Am. Oil Chem. Soc.*, *24*, 325–327 (1947).

[25] W. S. Mueller and M. J. Mack, *Massachusetts Expt. Sta. Ann. Rept., 1939*, 42.

machinery, which continuously feeds the raw food into the kettle and withdraws and drains it after a predetermined cooking period.

The temperature employed in deep frying varies from about 325–350°F., in the frying of nuts or potato chips, to about 375–390°F. in doughnut frying. At these temperatures fats hydrolyze appreciably in the presence of water. As all of the foods which are commonly fried are more or less wet, fats used for frying exhibit a progressive increase in their content of free fatty acids. Some polymerization also takes place during the frying operation, as is evidenced by a gradual accumulation of gummy material on the bottom or edge of the frying kettle. However, the loss of oil, through either polymerization or volatilization of decomposition products is very small, *i.e.*, of the order of 0.2–0.3% of the total fat used.[26]

Since frying is always conducted with the surface of the fat freely exposed to the air, it might be supposed that the fat would rather quickly become rancid while in use. Such, however, is not the case. While the exposure of fat to oxygen at high temperatures will certainly impair its stability, it does not appear that fat is capable of actually becoming rancid while it is very hot. The high temperatures prevailing in the frying kettle prevent the formation of peroxides, and apparently otherwise break up the reactions leading to the development of true rancidity. Also the continual vaporization of water from the surface of the frying food provides a kind of continuous steam distillation, which seems to remove volatile substances from the fat, and probably contributes to maintaining it in a nonrancid and relatively flavorless and odorless condition. For frying potato chips, nuts, and other foods which are packaged and not immediately consumed, relatively stable fats, such as coconut oil and all-hydrogenated vegetable shortenings are preferred. For doughnut frying, however, and for general use in restaurants and hotels, fats of ordinary stability, such as compound-type shortenings and cooking oils, are satisfactory. Products containing much soybean oil, either raw or hydrogenated, are generally avoided by deep fryers, because of the pronounced tendency of this oil to undergo heat-induced flavor reversion.

When a fat is heated to a high temperature, its tendency to smoke is in direct proportion to its content of free fatty acids. At a frying temperature of 390°F., smoking will occur if the fat contains more than about 0.1% of free acids. Although the shortenings and cooking oils of the highest grade are manufactured with free fatty acids not exceeding 0.03%, this low initial acid content is not maintained with even slight use of the fat. Most commercial deep frying is actually conducted in fat containing 0.5% or more of free acids. Consequently, all fats can be expected to smoke considerably in commercial use. Obviously, minor differences in

[26] S. W. Arenson and E. G. Heyl, *Oil & Soap*, *21*, 60–62 (1944).

the initial smoke points of different fats are of little practical significance.

The data recorded in Table 83 are typical of small-scale doughnut frying tests in which no fat is added to the kettle during the course of the test. In this test an initial charge of 15 pounds of fat was used for frying on 11 successive days. The frying period during each day was approximately 2 hours, and the fat was allowed to cool after each day's use.

TABLE 83

DOUGHNUT FRYING TEST[a] WITH ALL-HYDROGENATED VEGETABLE OIL SHORTENING
(IODINE VALUE = APPROXIMATELY 62)

| Days | Frying time, hrs.: min. | | Doughnuts fried, total no. | FFA, % | Fat | |
	Daily	Cumulative			Peroxide value[b]	Flavor and odor
0	0	0	0	0.02	2	Good
1	2:20	2:20	46	0.07	7	Good
2	2:00	4:20	91	0.11	7	Good
3	2:00	6:20	132	0.18	8	Good
4	2:10	8:30	174	0.25	8	Good
5	2:00	10:30	228	0.32	9	Good
6	2:05	12:35	283	0.47	9	Good
7	2:00	14:35	341	0.60	5	Good
8	2:00	16:35	394	0.70	5	Good
9	2:40	19:15	447	0.95	5	Good
10	3:00	22:15	507	1.10	5	Good
11	2:45	25:00	559	1.23	5	Good

[a] 15 pounds of fat, 14 inch kettle, at 385°F.
[b] Milliequivalents per 1000 rams fat.

Very extensive deep frying tests, involving the use of commercial doughnut machines, and the preparation of nearly 200,000 doughnuts have been reported by Lantz and Carlin.[27] Five different shortenings were used in the tests; three of the shortenings were of the all-hydrogenated variety, and two were of the compound type, and contained about 80% of unhydrogenated cottonseed oil. The machines were operated continuously 14 hours a day, for a total frying time of 100 hours. Fresh fat was added hourly to replenish that absorbed by the doughnuts. Under the condition of the test, the different fats reached in about 80 hours an equilibrium-free fatty acid content varying from 0.70 to 1.35%. All of the fats darkened greatly during the test, their Lovibond red colors increasing from 1.5–3.5 units to 20–30 units. There was no correlation between the original colors of the fats and their final colors. The compound type shortenings, as a group, exhibited no greater tendency to develop free fatty acids than the all-hydrogenated shortenings, although they were slightly more inclined to form gum. It was concluded that compound type shortenings are not significantly less satisfactory for deep frying than all-hydrogenated products.

[27] C. W. Lantz and G. T. Carlin, Oil & Soap, 15, 38–41 (1938).

The experiments of Arenson and Heyl,[28] carried out in commercial deep frying equipment with corn oil, blended corn oil, and cottonseed oil shortenings, and all-hydrogenated cottonseed oil shortening, substantiate the findings of Lantz and Carlin that the fat absorption of doughnuts is virtually the same for all fats, regardless of their degree of unsaturation, and that the absorption is also independent of the free fatty acid content, at least up to a level of 0.6%. The equilibrium free fatty acid level in the kettle during their tests was progressively higher with decreased unsaturation of the fat, being approximately 0.25% for corn oil (iodine value, 122), 0.28% for a blended shortening of iodine value 106, 0.45% for a blended shortening of iodine value 85, and 0.55% for an all-hydrogenated shortening of iodine value 60. However, these differences were not considered to be of great practical significance. Actually, a fresh fat of low free fatty acid content does not produce doughnuts of good shape and color; a breaking-in period is required during which surface-active materials are developed, before a new fat charge produces an entirely satisfactory product. Apparently, surface-active substances other than free acids are involved, inasmuch as different fats begin to function satisfactorily at different levels of acidity. In the case of the fats tested by Arenson and Heyl, these levels were 0.1% for the corn oil and the blended product of high iodine value, 0.25% for the blended shortening of lower iodine value, and 0.35% for the all-hydrogenated shortening.

With prolonged usage of frying fats, trouble may be encountered with foaming. It is claimed that foaming may be minimized by special treatment of the fat during its manufacture, and also by the addition to it of certain surface-active substances.[29] Shortenings containing substantial proportions of coconut oil or other lauric acid oils are particularly noted for their foaming properties, which restrict their usefulness in frying foods of high moisture content. It has recently been demonstrated by Naudet and co-workers[30] that foaming is not characteristic of oils of low molecular weight alone, but is the result of mixing oils containing fatty acids of considerably different chain lengths. It was found, for example, that coconut oil alone did not foam, nor did peanut oil, but foaming occurred in mixtures of the two containing 10 to 95% coconut oil. Hence, foaming is inherent in virtually any fat containing much coconut oil, and the tendency toward this fault cannot be materially reduced except by reducing the coconut oil content to a very low level.

[28] S. W. Arenson and E. G. Heyl, *Oil & Soap, 20*, 149–151 (1943).
[29] See H. C. Black (to Industrial Patents Corp.), U. S. Pats. 2,320,319 and 2,322,186–187 (1944); and also H. E. Robinson, H. C. Black, and H. S. Mitchell, *Oil & Soap, 17*, 208–210 (1940).
[30] M. Naudet, O. Micaelli, and P. Desnuelle, *Bull. mens. Inst. tech. études et recherches corps gras, 1948*, No. 6, 32–35.

D. Varieties of Baked Goods

1. BREAD AND ROLLS

Bread is one of the lowest of all baked products in fat content. The average amount of fat included in bread dough is between 2 and 3%, although it has been claimed[31,32] that the quality of bread is improved by increasing its fat content to 4% or even 6%. A typical formula for white bread is as follows (in parts):

Flour	55.0
Milk	37.5
Shortening	3.0
Sugar	2.0
Yeast	1.5
Salt	1.0
Total	100.0

Unlike most other baked products, bread does not absolutely require fat in its composition. A reasonably good bread can be made without the assistance of any fat other than the small amount of wheat oil present in the flour, and French bread and hard rolls are often so made. However, the use of a small quantity of shortening not only increases the volume of the bread loaf, but also yields a sponge which is more easily broken up, as well as a smoother dough, and a bread with a more tender crumb.[33] Soft rolls commonly contain more shortening than bread, i.e., 3–6%.

Baker and Mize[34] have noted the action of shortening materials in bread in connection with an investigation of the changes occurring in bread dough during the process of baking. In the course of baking they found that the dough began to become strengthened at a temperature of 136°F. because of "starch swelling." The swelling abstracts water from the gluten in the dough and makes it both stronger and more elastic. The final strengthening of the dough is due, of course to coagulation of the gluten, which begins at 165°F. There is a critical period between about 100° and 136°F., however, when the dough is very soft, and apparently more or less permeable to gases. Bread made without shortening, or bread shortened with liquid oils was observed to be deficient in volume because of its failure to retain leavening gases during this critical softening period. The unshortened or oil-shortened loaves were of good texture and a good cell structure; there was no evidence of the loss of gas being due to rupture of the cells. It was concluded, therefore, that plastic fats gave loaves

[31] G. F. Garnatz, Oil & Soap, 12, 290–293 (1935).
[32] W. L. Heald, Cereal Chem., 16, 817–820 (1939).
[33] B. Sullivan, Cereal Chem., 17, 666–667 (1940).
[34] J. C. Baker and M. D. Mize, Cereal Chem., 16, 682–695 (1939).

of high volume due to their being able in some way to inhibit the diffusion of gas through the cell walls.

Probably the mechanisms mentioned previously in connection with cake leavening apply also in some degree to the leavening of bread. In other words, cleavage of the dough to form gas-filled cells probably is inclined to take place at places where the continuity of the dough is broken by layers of fat. This would tend to leave the cell walls coated with films of fat which would undoubtedly decrease their porosity. Liquid oils do not form fat layers or films in the dough, but are formed into spherical globules by forces of surface tension (see Figure 40), which become very powerful as the fat is finely dispersed.

Although various plastic fats are used for shortening bread, the material which enjoys much the widest use is lard. Many bakers consider that it contributes in a desirable way to the flavor of the product. Lard also has the advantage of being relatively soft and easily handled.

Appreciable quantities of fat are used in commercial bakeries for greasing bread pans. As the pans are but infrequently washed, this particular service requires a fat which is not only easily applied, but is also not inclined to become gummy with long continued use. The preferred fat for the purpose is lard oil, prepared by removing the higher melting portions of ordinary lard, by means of fractional crystallization.

2. YEAST-RAISED SWEET GOODS

A variety of buns, rolls, coffee cakes, etc., are made from a yeast-leavened sweet dough containing 10% or more of sugar. Such sweet doughs require considerably more shortening in their preparation than do ordinary bread doughs. The average content of fat in yeast-raised sweet doughs is perhaps 10%. The following is a typical formula for this variety of dough (in parts):

Flour..........................	47.0
Milk..........................	21.0
Shortening....................	10.0
Sugar........................	10.0
Whole eggs...................	7.5
Yeast........................	4.0
Salt..........................	0.5
Total.......................	*100.0*

The shortening agents used in the manufacture of this class of goods include lard, butter, and compound and all-hydrogenated shortenings. The creaming qualities of the fat are not as important in this application as they are in making cakes; but the flavor is of some importance; and it is important that the fat be plastic and capable of being well dispersed in the dough. Superglycerinated shortenings, because of their ability to

become highly dispersed, are claimed to produce sweet yeast goods of superior texture and tenderness. The use of shortening materials containing mono- and diglycerides in this class of products is patented.[35]

3. SODA CRACKERS

Soda crackers usually contain from 7 to 10% of fat, which is necessary to impart to the product its characteristic flaky structure. The following is a typical soda cracker formula (in parts):

Flour	68.5
Water	22.0
Shortening	8.0
Salt	1.0
Soda	0.3
Yeast	0.2
Total	*100.0*

Although the shortening value of a fat which is to be used in crackers is an important consideration, the chief emphasis in the selection of a fat for this purpose is placed upon stability. Soda crackers, unlike bread and many other products, cannot be baked in small establishments and distributed locally, with a quick turnover in sales and consumption. On the contrary, the complicated and expensive machinery required for making crackers has largely confined the manufacture of this commodity to a relatively few large establishments. Crackers are now sold almost exclusively in small, individual packages, which may be stored for months in warehouses or on dealers' shelves before the contents are consumed.

The broad subject of the stability of fats in baked products has been discussed in a preceding paragraph (page 305). As mentioned previously, soda crackers are more liable to become rancid than other packaged products because they contain no sugar to serve as an antioxidant for the fat which they contain.

The most stable fats available for cracker manufacture are all-hydrogenated shortenings of the special biscuit and cracker type. Such shortenings have a stability, as measured by the A.D.M. method, of 120 hours or more, as compared with 8 to 12 hours for most lards and oleo oils. However, crackers made with biscuit and cracker type shortening will not keep ten times as long as those made with lard or oleo oil. The baking process appears to destroy some of the natural antioxidants which are partly responsible for the high stability of vegetable shortenings. Also, the acceleration of oxidation by heat appears to exaggerate the superiority of the more stable fats. Altogether, both on the basis of laboratory work and practical experience, it appears more probable that crackers made

[35] A. S. Richardson, H. S. Coith, and V. M. Votaw (to Procter and Gamble Co.), U. S. Pat. 2,132,700 (1938).

with the better vegetable shortenings will keep two to four times as long as those made with ordinary lard.

In spite of the availability of vegetable shortenings of extremely high stability, most crackers are made with lard, partly, at least, because of its lower price. Many crackers are also made with oleo oil. Compound type shortenings are not sufficiently stable to be much used in cracker manufacture. Because of their poor stability in baked products and their lack of shortening power, cooking oils are seldom if ever used.

A considerable part of the highly stable vegetable shortening entering packaged bakery products is probably used in admixture with lard or other fats of lower stability, inasmuch as even a small proportion may improve the keeping quality of the products considerably.[15]

A small unsweetened cracker of high fat content has recently become popular in the United States. These crackers, which are marketed under various proprietary names, are enriched by a coating of fat sprayed on their surface. In the manufacture of these crackers any plastic fat may be used in the preparation of the dough, but the preferred coating fat is coconut oil, which imparts to the surface a characteristic glossy appearance.

4. CAKES

While the volume of cake produced in any year is much below the production of bread, the cake baking industry is an important consumer of shortening materials because of the relatively high percentage of fat used in cake formulas. The total production of cake is of course much larger than the portion produced in commercial bakeries. As long ago as 1935, Bailey and Le Clerc[36] estimated that the flour made into cake in the United States amounted to 5,500,000 barrels each year (out of a total of 110,000,000 barrels) and that each barrel produced over 800 pounds of cake. Computed upon this basis, the actual production of cake would be between 4 and 5 billion pounds. The fat consumed in this amount of cake would amount to something over 500,000,000 pounds. Of the total amount of cake baked, it was estimated that 20 to 25% was made by commercial bakers. It is probable, however, that the ratio of commercially baked to home baked cake has increased since that time.

Cake is distinctive among baked products for its combination of extreme sweetness with a highly developed cellular structure. To dissolve the large proportion of sugar used in its composition, cake dough must contain a high percentage of liquids. Hence cake doughs are thinner and more fluid than those of other classes of baked goods. In order for the relatively watery cake dough to rise and assume the desired form in the baking operation, its structural requirements are extremely critical. As

[36] L. H. Bailey and J. A. Le Clerc, *Cereal Chem.*, *12*, 175-212 (1935).

explained previously, the shortening used in a cake plays a predominant role in determining this structure. Consequently, the quality requirements for cake-making fats are much more exacting than for fats which are to be used for most other baking purposes.

The cakes which contain fats may be divided into two main classes, namely yellow cakes, in which whole eggs or egg yolks are used, and white cakes, which are made only with egg whites. The two classes differ considerably, both in the characteristics of the finished products and the behavior of their doughs. The so-called "sponge cakes" constitute a third class, but as these are made without the use of shortening, they are outside the scope of the present discussion.

The essential ingredients in a yellow cake are flour, sugar, shortening, and whole eggs or egg yolks. Small quantities of salt and flavoring extracts are used for flavor, and unless a very high percentage of eggs is used, milk is also added, to provide the necessary amount of liquids in the dough. Baking powder or a similar leavener is used in all cakes except the higher fat content pound cakes. Based on 100 parts of flour, the approximate range within which the other major ingredients may be varied is as follows:

Flour	(100 parts)
Sugar	80–140
Shortening	20–100
Eggs	20–100
Milk	0–100

There are a number of reasons why the above proportions must be adhered to. In order that the cake may be characteristically "rich" in taste, and not "bready," the shortening content must be fairly high. Usually it is not less than about 35% of the weight of the flour, or more than about 50%. In cakes of the pound cake type, however, the fat content may amount to as much as 100% of the weight of the flour.

Practically all cake formulas require an amount of eggs equal to or greater than the amount of shortening. The use of an excess of shortening with too little eggs produces a poor dispersion of fat in the dough, with consequent impairment of volume and texture in the finished cake. Cakes with an excessively high ratio of fat to eggs are also inclined to give the impression of greasiness. An excess of eggs much beyond that required by the shortening is seldom used, because eggs are normally the most expensive ingredient in the dough. Pound cakes, which are very rich in fat, are correspondingly high in egg content.

The proportions of milk and eggs in a cake formula are related, since both are liquid ingredients. When the fat in the mixture consists of ordinary shortening, the weight of milk is usually about equal to the weight of eggs. In a very rich pound cake formula, the milk may be re-

duced much below the weight of the eggs, and in formulas for superglycerinated fats the milk may exceed the eggs in amount by as much as 100%. With ordinary shortenings the usual proportion of liquids (eggs and milk combined), is about 100% of the weight of the flour. With superglycerinated shortenings the liquids may be increased to as much as 165% of the weight of the flour. A cake containing too little liquids will not only be dry and unpalatable, but also will have a harsh texture. If too great a quantity of liquids is used in the cake, the structure will be unduly weakened, and it will be likely to fall or collapse in the oven.

The amount of sugar that can be used is determined by the liquid content of the cake. In no case can the sugar exceed about 85 to 95% of the combined eggs and milk, as starch in the flour will fail to gel in the presence of stronger sucrose solutions.[37] The strong emulsifying properties of the superglycerinated shortenings contribute to the strength of the dough sufficiently to permit the incorporation of sufficient liquids to make the sugar content equivalent to as much as 140% of the weight of the flour. Cakes made with a high ratio of sugar to flour are commonly termed "high-ratio" cakes. The maximum amount of sugar which can be incorporated in a cake depends to some extent upon the form in which the cake is to be baked. Thin layers and sheets require less structural strength, and may contain more liquids and sugar than loaves or other relatively thick forms.

Typical formulas for different varieties of high-quality cakes are shown in Table 84. Various optional ingredients, such as nuts, fruits, spices, chocolate, etc., may, of course, be incorporated in the basic cake doughs.

TABLE 84

TYPICAL FORMULAS (PARTS BY WEIGHT) FOR DIFFERENT VARIETIES OF CAKES

Ingredient	Ordinary yellow cake	High-ratio[a] yellow loaves	High-ratio[a] yellow layers	Pound cake	Ordinary white cake	High-ratio[a] white layers
Sugar	25.5	29.6	29.8	24.6	25.8	29.3
Fat	13.4	11.4	11.6	20.0	13.0	11.5
Eggs[b]	14.8	11.4	12.6	24.6	17.8	15.7
Milk	14.8	22.5	22.2	5.0	15.4	20.0
Flour	29.8	22.5	21.2	24.6	25.8	20.9
Baking powder	0.7	1.3	1.3	—	0.9	1.3
Salt	0.6	0.8	0.8	0.7	0.6	0.8
Flavor	0.4	0.5	0.5	0.5	0.5	0.5
Total	100.0	100.0	100.0	100.0	99.8	100.0

[a] Suitable for use with superglycerinated shortenings.
[b] Whole eggs for yellow cakes and pound cake; egg whites for white cake.

[37] See S. Woodruff and L. Nicoli, *Cereal Chem.*, 8, 243–251 (1931).

Formerly, cakes were commonly made, either in the commercial bakery or in the home, by the so-called "sugar batter" method, wherein the fat and sugar were first creamed together, the eggs were then added as creaming was continued, and finally, the flour and milk were mixed in, in alternate small portions. The lightness of the finished cake depended to a large extent upon incorporating a large volume of air in the creaming process, which, without the aid of suitable mixing equipment, was quite laborious. As an alternative method, particularly for white cakes, a "flour batter" method was used, which involved creaming the flour with the fat and then adding the eggs and sugar, which were beaten in a separate bowl.

With superglycerinated shortenings, the mixing procedure is considerably simplified. The recommended method for bakery practice is to cream the flour and fat, then mix in the sugar and part of the milk, and lastly, add the eggs and the remainder of the milk. In none of the stages need the mixing be done with great care, nor need it be at all prolonged. A slightly modified procedure for household cake making is to mix the flour, sugar, and eggs with one-half to two-thirds of the milk, and then incorporate the remainder of the milk and the eggs in the same bowl. This so-called "quick-mix" method, which requires but a single mixing bowl, and eliminates the drudgery of prolonged hand mixing, has contributed greatly to the popularity of superglycerinated shortenings for household use.

Cakes made to a high-ratio formula, with the use of large proportions of sugar and milk, possess a number of points of superiority over ordinary cakes. They are sweeter, more tender, and moister, and they dry out less rapidly. Also, since sugar and milk are relatively cheap, they are less expensive to make. Their disadvantages are that they are relatively fragile, and that they are too light and fluffy and too sweet for some tastes. Regardless of the merits of the high-ratio formulas, however, there can be little argument as to those of the superglycerinated shortenings, as these materials will produce a cake of superior grain and texture when used in any formula. The high degree of fat dispersion obtainable with a superglycerinated shortening in a non-high-ratio dough as compared with that obtainable with an ordinary shortening, is evident from a comparison of Figures 37 and 45.

From a purely physical standpoint, butter is not a superior cake-making material. It does not cream particularly well, and is notably lacking in uniformity. On the score of flavor, however, butter has no satisfactory substitute. The use of butter in a cake imparts a desirable flavor to the product which is impossible to obtain with any other shortening material. It is noteworthy that margarines which simulate butter very closely when used as table spreads, fail to impart any considerable amount of butter

flavor to cake or other baked products. For cake baking, relatively strong flavored butters are preferred, such as would not ordinarily be considered most desirable for table use.

Tastes differ so greatly that it is difficult to say what constitutes the best shortening material for cake baking. However, it is the opinion of at least a good many bakers that a superior product is obtained with a mixture of superglycerinated shortening and butter, in a formula which contains more sugar than the older commercial recipes, but somewhat less than the true high-ratio formulas.
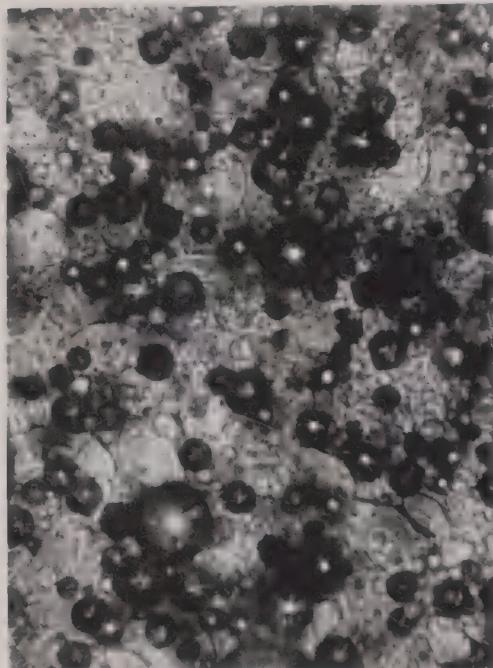
Fig. 45. Photomicrograph (×290) of pound cake dough made with supergly-cerinated shortening.
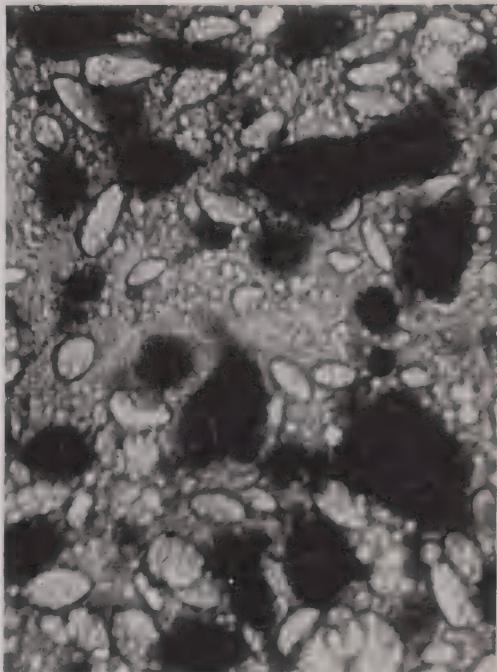
Fig. 46. Photomicrograph (×290) of yellow cake dough made with lard.

Salad and cooking oils are inapplicable to cake making, except for certain types of modified sponge cakes. Oleo oil is seldom used, principally because of its short plastic range. Margarine, for the reasons stated above, possesses little or no advantage over ordinary shortenings. Shortenings of the all-hydrogenated, and to a lesser extent the compound, types have been much used in the past by commercial cake bakers, but have now been supplanted to a large extent by superglycerinated shortenings. The use of these shortenings and certain related materials in cake making is

covered by patents.[30,38-40] Nonsuperglycerinated shortenings can be used in high-ratio formulas employing sorbitol derivatives (see page 400) as emulsifying agents.

In the case of all-hydrogenated vegetable oil shortenings, those made wholly or largely from cottonseed oil are generally considered to produce cakes of better volume than those in which soybean oil predominates.[40a]

Ordinary lard, because of its flavor and its poor creaming properties, is seldom used for cake making, but the newer deodorized lard products have attained some popularity for this purpose.

5. Sweet Biscuits, Wafers, and Cookies

The various commercially baked cookies, wafers, sweet biscuits, etc., are all quite similar in structure and appearance. They consist of thin, crisp products, of low moisture content, which are baked from a stiff, sweet dough. The dough is either rolled into a thin sheet, from which the individual biscuits are cut, or else is extruded through a die and sliced into thin sections by a wire cutter. Most retail bakeries do a considerable volume of business in cookies and similar products. In addition to the fat used by the smaller bakeries in this class of goods, great quantities of fats are consumed by large manufacturers of packaged sweet goods, whose output includes a wide variety of items, with and without fruit, cream, and other fillings and coatings.

The essential difference between these products and ordinary cake is their low content of moisture. Whereas the sugar in ordinary cakes is in the form of a liquid and mobile syrup, that in cookies may be solidified to a candylike mass. Sufficient fat must be present to break the continuity of this mass; otherwise the product will be impossibly hard and refractory. Most cookies, etc., contain about the same proportions of fat as yellow and white cakes, namely 10 to 15%.

It is desirable for the fat to contribute some degree of leavening of this class of products. However, the leavening is much less critical than in the case of cakes, and in choosing a shortening for biscuits and cookies the chief emphasis is placed upon shortening value and stability, rather than creaming and emulsifying properties.

The fats which are used for these products are principally lard, oleo oil, and all-hydrogenated vegetable shortenings. Lard has the advantage of being high in shortening value, whereas oleo oil and all-hydrogenated shortenings have the advantage of being more stable than lard.

[38] H. S. Coith, A. S. Richardson, and V. M. Votaw (to Procter and Gamble Co.), U. S. Pats. 2,132,396–97 (1938).
[39] B. R. Harris, U. S. Pats. 2,024,357 (1935) (to Procter and Gamble Co.); 2,132,416 (1938); 2,132,417 (1938); 2,132,687 (1938).
[40] B. R. Harris (to Procter and Gamble Co.), U. S. Pat. 2,158,775 (1939).
[40a] See S. W. Arenson, Food Inds., 22, 1015–1020 (1950).

6. PIE CRUST

Pie crust consists essentially of flour and fat, mixed with a little salt and water. However, in some commercial formulas small proportions of sugar and eggs are used. The amount of fat in the formula may vary from as little as 20% to as much as 60% but in commercial products of the best quality is usually in the neighborhood of about 40%. A liberal proportion of fat in the dough not only makes the crust tender, but also prevents it from readily becoming soggy, from absorption of the watery ingredients of the pie filling.

Most pie crust is of the so-called "flaky" variety. In making this variety of pastry, a fine dispersion of the fat throughout the dough is not desired —on the contrary, it is essential that the dough be but slightly mixed, in order that the fat may be incorporated in the form of relatively large masses. When the dough is rolled out into a sheet the fat is pressed into the form of flat layers, dispersed along parallel planes through the crust. After the crust is baked, these layers of fat provide planes of cleavage parallel to the surface of the crust. The crust is consequently inclined to disintegrate in the form of flakes rather than crumbs. Obviously a plastic fat is required for making a flaky pie crust. A "crumbly" crust is also sometimes prepared, by using a very high proportion of fat or even a liquid oil, and mixing the fat and flour very thoroughly. This produces a fragile crust in which the surfaces of cleavage are neither plane nor parallel, but extend in all directions.

The requisites of a good pie crust shortening are plasticity and a high shortening value. Ability to cream, ability to emulsify, and stability are unimportant. Lard is much used for pie crust. It is superior to most other fats in shortening power, and in pies its characteristic odor and flavor are considered desirable by many bakers. The new deodorized lard shortenings also have good shortening qualities in pie crust, and have the advantage over ordinary lard of having neither flavor nor odor, in cases where a completely neutral product is desired. Compound type and all-hydrogenated shortenings are also used in considerable quantities in pie crust.

7. DANISH AND PUFF PASTRY

The manufacture of puff pastry and pastry of the Danish type requires a shortening material of a somewhat special variety. In these products, the distribution of fat in the dough is somewhat similar to that in ordinary flaky pie crust. However, this distribution is attained, not by mixing the fat in the dough, but by rolling it in after the dough is mixed.

The original dough may vary considerably in composition, and may or

may not be yeast-leavened. It is essential, however, that it have the property of ready extensibility, *i.e.*, it must be soft enough to roll out readily, but tough and coherent enough so that the rolled sheets will not easily tear or come apart in rolling and handling. Generally no large amount of fat is used in making up the original dough, but it is usual to roll in a quantity of fat greater in amount than the dough in which it is incorporated, so that the finished product is very high in fat content.

The "rolling in" operation is initiated by forming the dough into a thin, roughly rectangular sheet. Then, beginning at one end of the sheet, a layer of fat is spread over two-thirds of its surface. The ungreased third of the sheet is then folded over on the middle portion of the sheet, and the remaining one third, which has been covered with fat, is folded on top of the ungreased surface. This operation produces a new sheet, consisting of three layers of dough, separated by two layers of fat. The new sheet is then rolled out to the size of the original sheet, the latter is again spread with fat and folded, and the rolling, fat spreading, and folding is continued for a number of times.

As each complete cycle of operations increases the number of layers threefold, the ultimate result is a laminated sheet, consisting of a great many very thin alternate layers of fat and dough. When the product is baked, the layers of dough tend to separate, from the expansion of air or water vapor entrapped between them. This produces a leavening action, and causes the product to rise in the oven.

In making this variety of pastry the best results are obtained with special pastry margarines or puff pastry shortenings, which have been compounded to yield a tough, waxy fat, of good extensibility. For the manufacture of pastry shells of the puff-pastry type, the use of special "puff paste" is more or less essential. For certain sweet pastries, however, in which a yeast-leavened dough is used, and in which it is not necessary for the layered structure of the product to be so precisely developed, any one of a variety of fats may be used, including margarine, butter, lard, and the vegetable shortenings.

8. Doughnuts and Other Fried Products[40a]

Doughnuts, crullers, and related products comprise a class of goods which are not baked in an oven, but are deep-fried in hot fat. In the United States, much the greater portion of these products consists of doughnuts, although in some sections of the country there is a considerable production of crullers and of fried pies.

Little fat is used in the preparation of doughnut or cruller dough, but the dough will absorb a considerable quantity of fat in frying. The usual

fat content of doughnuts is in the neighborhood of 15%; that of potato chips is about 40%.

The subject of commercial food frying has been discussed at some length in previous paragraphs, Section C,2). It may be said here, in summary, that the chief considerations in the choice of a frying fat are good flavor stability at frying temperatures, and, in the case of packaged products, a high resistance toward oxidation. A few of the latter may be properly classed as bakery products, although much the most popular fried packaged product in this country is potato chips. A relatively low melting point is desirable, to avoid the deposition of a visible layer of fat crystals on the food. Furthermore, since the flavor stability of hydrogenated soybean oil is not satisfactory, the best fat for commercial frying on all counts is generally considered to be a cottonseed oil or peanut oil product selectively hydrogenated to produce a shortening similar to or identical with the so-called biscuit and cracker or high-stability shortenings.

In doughnut frying the crystallization behavior of the fat is more important than in the frying of other products; inasmuch as it should neither deposit crystals in sufficient quantity to give the doughnut surface a dull appearance, nor be so soft as to soak a sugar coating with oil.

The extent to which frying fats are absorbed by doughnuts and other fried products is a matter of some importance; as stated previously, however, the best opinion appears to be that there are actually no significant differences among different edible fats in this respect. The tests of Lantz and Carlin,[27] referred to above, showed the fat absorption per dozen doughnuts (about 12 ounces) to vary from 1.646 to 1.792 ounces with five different shortenings. However, the differences were attributed to the presence of unavoidable variables in the frying operation. In the more closely controlled tests of Arenson and Heyl[28] the fat absorption varied only from 3.02 to 3.09 grams per doughnut with four widely different varieties of fat, corresponding to 1.2 ounces per one dozen 10-ounce doughnuts.

Lantz and Carlin state that the fats that they tested showed wide variations in absorption during the first four days that they were used, after which their rates of absorption became more or less constant. Thus it appears that the tendency of a fat to be absorbed in doughnut frying cannot be evaluated except upon the basis of extended tests.

9. Cream Icings

Considerable quantities of fat are consumed by commercial bakers in the manufacture of cream icings, for cakes and similar goods. This product consists basically of fat, powdered sugar, and milk, with a consid-

erable quantity of air beaten into the fat. The following formula (in parts) is typical of cream icing in its simplest form:

Fat	25.0
Powdered sugar	50.0
Milk	23.8
Salt	0.6
Flavor	0.6
Total	*100.0*

The fat most commonly used for cream icings is an all-hydrogenated vegetable shortening, to which butter is sometimes added for flavor. Superglycerinated shortening produces an icing which is smoother and more stable than ordinary shortening. Shortenings of the compound type are usually not sufficiently neutral in flavor for good cream icings. Lard is unsuitable for icings, both because of its flavor and its lack of creaming ability. A deodorized lard product which has been stiffened by hydrogenation or the addition of highly hydrogenated lard may be used satisfactorily. The fat used in cream icings must be sufficiently firm to remain plastic at the highest temperature to which the icing is to be subjected, as the body of the product depends upon the plastic properties of the fat.

Cream icing is essentially an emulsion of sugar syrup, sugar crystals, fat, and air; according to the formula, the fat may be either the continuous or the discontinuous phase.

10. Biscuit Fillings and Coatings

Certain varieties of packaged sweet biscuits are prepared with coatings which have a fat base. For this purpose a fat with a short plastic range is desirable. The biscuits will retain their form and appearance better in the package if the fat is quite firm or even hard at ordinary temperatures. However, it must melt, or at least soften readily in the mouth. Thus the fats which are most suitable for this purpose are similar in properties to confectioners' fats rather than the plastic fats previously described.

Various so-called "enrobing" fats for biscuits are marketed under proprietary names. Their formulas are generally secret; however, many of the newer products are based largely or entirely on normally liquid oils hydrogenated to the proper consistency.

11. Prepared Mixes

Within recent years, a large retail trade has grown up in this country in dry packaged mixes containing flour, sugar, milk solids, shortening, flavor, and a leavening agent, which need only to be mixed with water or milk, and in some cases, eggs, to yield a batter ready for baking into cakes, rolls, biscuits, etc. All-hydrogenated shortenings or antioxidant-

treated lard products of relatively high stability, which are often "tailor-made" to the individual manufacturer's specifications, are usually used in these products.

E. Confectioners' Fats

Most of the fat consumed in candies consists of cocoa butter. Chocolate, which is the product obtained by grinding roasted cocoa beans, contains approximately 50% of fat, and 50% of solid material. In the manufacture of chocolate candies, the solids content of the chocolate is greatly increased by the addition of sugar; hence in order to maintain a suitable consistency in molten chocolate coatings it is necessary to add fat beyond the amount normally present in the chocolate.[41] The amount of fat added may vary from 15 to 25% in ordinary coatings, to 35% or more in milk chocolates. In the case of candies which are labeled as chocolates, the added fat must be pure cocoa butter; cheaper products such as five-cent candy bars, which are not designated as chocolates, may contain less expensive fats. The coating fats used in the United States as substitutes for cocoa butter consist principally of hydrogenated palm kernel oil products and stearines pressed from coconut, palm kernel, or other lauric acid oils. In Europe there is some use of Borneo tallow and other less common vegetable butters. A very short plastic range is of course essential in a coating fat, as the coating must be nongreasy at ordinary temperatures, but must melt in the mouth.

The commercial machine coating of candies is quite critical insofar as the properties of the coating fats are concerned, inasmuch as the coatings must be capable of being quickly transformed from viscous, semiplastic suspensions to hard, nongreasy solids. The crystallization habits of the fat, the rapidity with which it solidifies, its tendency to supercool, the temperatures at which it melts and solidifies, its tendency toward polymorphism, are all extremely important. Fats other than cocoa butter, or fat mixtures, behave differently from pure cocoa butter, and require corresponding adjustments in the coating process. Occasional lots of cocoa butter are encountered which exhibit a sufficiently abnormal behavior to cause trouble in the coating procedure applicable to normal cocoa butters. For the evaluation of cocoa butter and other coating fats dilatometric examination or the standard solidification test proposed by Jensen[42] is recommended.

In the case of chocolate confections which are to be molded, the volume

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[41] The addition of lecithin to the coating reduces its viscosity and minimizes the amount of fat which must be added. For a complete discussion of the surface activity of lecithin in chocolate suspensions, see R. Whymper, *The Problem of Chocolate Fat Bloom*, Manufacturing Confectioner Pub. Co., Chicago.

[42] H. R. Jensen, *The Chemistry, Flavouring, and Manufacture of Chocolate Confectionery and Cocoa*. Blakiston, Philadelphia, 1931.

change of the fat upon solidification is important since a considerable shrinkage is necessary for good molding properties. In addition to the coating fats consumed in candies, considerable quantities of fats of this type are also used in coating ice cream bars and sweet biscuits.

Although the coating fats comprise the most important group of confectioners' fats, there is a considerable consumption of other fats in candies. Cocoa butter, coconut oil, oleo oil, and butter comprise some of the materials used. A few manufacturers of hydrogenated vegetable oils prepare special confectioners' fats. One of these consists of oil hydrogenated selectively to obtain a short plastic range, but with a melting point substantially above that of ordinary hydrogenated shortenings. This product is said to be particularly suitable for the manufacture of caramels.

SOAP AND OTHER SURFACE-ACTIVE AGENTS[1]

A. Introduction

There are a variety of oil and fat derivatives which owe their industrial importance to their ability to modify the surface behavior of liquids in which they are dissolved. These products may be grouped under the broad designation of "surface-active materials." According to their various uses, they are classified as detergents, wetting agents, emulsifying agents, dispersing agents, frothing agents, etc. The most important surface-active material is ordinary soap. Other materials derived from fats and oils include certain detergents other than soap, sulfonated oils for textile and leather processing, and a great variety of emulsifying and wetting agents which find special applications in many different industries.

Fats and oils, or rather fatty acids—for the latter are usually the essential materials—are peculiarly suitable for the production of surface-active agents because of their specific molecular structure. The commercially available fatty acids consist for the most part of straight hydrocarbon chains of 12 to 18 carbon atoms, terminating in a reactive carboxyl group. When the terminal hydrogen atom is substituted with an alkaline metal or when the carboxyl group is otherwise converted to a group of hydrophilic nature, the resulting molecule becomes endowed with certain peculiar properties. The hydrocarbon end then will have an affinity for fatty oils, aliphatic hydrocarbons, and similar long chain compounds, whereas the opposite end of the molecule, at some distance removed, will

[1] GENERAL REFERENCES: N. K. Adam, *The Physics and Chemistry of Surfaces,* 3rd ed., Oxford Univ. Press, London, 1941. J. Alexander, ed., *Colloid Chemistry,* Vols. I–VI, Chemical Catalog Co. and Reinhold, New York, 1926–1946. S. Berkman and G. Egloff, *Emulsions and Foams,* Reinhold, New York, 1941. A. Chwala, *Textilhilsmittel,* Springer, Vienna, 1939. D. Burton and G. F. Robertshaw, *Sulphated Oils and Allied Products,* Chemical Pub. Co., New York, 1940. W. Clayton, *The Theory of Emulsions and Their Technical Treatment,* 4th ed., Blakiston, Philadelphia, 1943. H. Freundlich, *Colloid and Capillary Chemistry,* trans. from 3rd German ed. by H. S. Hatfield, Methuen, London, 1926. H. Schönfeld, ed., *Chemie und Technologie der Fette und Fettprodukte,* Vol. IV, Springer, Vienna, 1939. G. S. Hartley, *Aqueous Solutions of Paraffin Salts,* Hermann, Paris, 1939. International Society of Leather Trades' Chemists, British Section, *Wetting and Detergency,* 2nd ed., Chemical Pub. Co., New York, 1939. A. M. Schwartz and J. W. Perry, *Surface Active Agents,* Interscience, New York, 1949. J. P. Sisley, *Index des Huiles Sulfonées et Détergents Modernes,* Teintex, Paris, 1949. E. G. Thomssen and J. W. McCutcheon, *Soaps and Detergents,* MacNair-Dorland, New York, 1949.

have an attraction for water or aqueous solutions. Thus within the same molecule there will be a dual affinity for substances of entirely different nature. Furthermore, the two ends of the molecule will be sufficiently separated for the two affinities to come into simultaneous and independent action.

The aforementioned dual nature of the molecule is an essential condition if the substance is to have surface activity, as will be more readily apparent from the ensuing discussion of the theory of surface action. In most cases, the size or length of the molecule is also somewhat critical, inasmuch as there must be a nice balance between hydrophilic and lipophilic properties in the molecule. If the chain is too long, there will be unbalance in the direction of a too great affinity for oily materials and insufficient affinity for water, accompanied by limited solubility in the latter. If the chain is too short, the compound will be relatively lacking in surface activity through an insufficiency of lipophilic properties. It is remarkable that in general the optimum chain length lies in the same range as that of the common fatty acids, i.e., 12 to 18 carbon atoms of about 18–25 A.

B. Theory of Surface Action

The modern theory of the mechanism of surface action is intimately related to the fundamental work of Harkins[2] and Langmuir[3] dealing with the phenomenon of molecular orientation at interfaces.

As mentioned previously, all substances capable of surface action are composed of relatively large molecules, which contain widely separated groups of dissimilar nature. It is also characteristic of these materials that they exert their useful effect in quite dilute solution. Their ability to function effectively in low concentrations is due to the tendency of the molecules to concentrate at interfaces between the solvent and solids, gases, or other immiscible liquids. At the boundaries of the solvent there is an orientation of the molecules according to the nature of the substances forming the interface. If the solvent is of an oily nature, the lipophilic hydrocarbon chain or "tail" of the molecule will be oriented toward the solvent, and the hydrophilic or polar "head" will be directed toward the other phase. If, as is more usually the case, the solvent is aqueous, the head of the surface-active molecules will be imbedded in the solvent phase and the tail will be directed outward. In a great many practical applica-

[2] J. Alexander, ed., *Colloid Chemistry*, Vol. I, Chemical Catalog Co., New York, 1926, pp. 192–264; Vol. V, Reinhold, New York, 1944, pp. 12–102; and Vol. VI, Reinhold, New York, 1946, pp. 1–76. Also W. D. Harkins, F. E. Brown, and E. C. H Davies, *J. Am. Chem. Soc.*, *39*, 354–364 (1917); W. D. Harkins, E. C. H. Davies, and G. L. Clark, *ibid.*, *39*, 541–596 (1917).

[3] See J. Alexander, *op. cit.*, Vol. I, pp. 525–546. Also I. Langmuir, *J. Am. Chem Soc.*, *39*, 1848–1906 (1917).

tions, the surfaces in question are those of two immiscible liquids, one of which is aqueous and the other oily. In such cases, the surface-active agent distributes itself at the interface, with the heads of the molecules in the water and "tails" in the oil.

When an interface is freshly established in the presence of a surface-active agent, the molecules of the latter must not only become properly oriented before they can function, but must also migrate to the interface from adjacent portions of the liquid. A sufficient degree of orientation and migration to establish equilibrium conditions may require an appreciable time. In practical applications, therefore, the speed with which an agent acts must sometimes be considered, as well as its ultimate effectiveness. The effectiveness of a surface-active agent under static conditions (with equilibrium established) may be somewhat greater than under dynamic conditions (which produce a series of constantly renewed interfaces).

The tendency of surface-active molecules or ions to migrate to the interface of a solution and there form an oriented or adsorbed film is, in qualitative terms, a manifestation of forces arising from the incompatibility of the hydrocarbon chain with water, which seek to expel this portion of the molecule from the body of the solution. In addition to producing adsorption at interfaces, these same forces also tend to produce aggregates of colloidal dimensions throughout the body of the solution. Within these aggregates there is the same orientation of molecules (or ions) as at a gross surface of the liquid, i.e., the "heads" are directed toward the surrounding water, whereas the "tails" are directed toward a common center, where they are literally "dissolved" in one another. The formation of colloidal micelles in solution is thus a general characteristic of surface-active materials.[4,4a]

In the older literature, great emphasis is placed on the colloidal nature of substances which are effective as emulsifying agents, deflocculating agents or "protective colloids," detergents, etc. Actually, the colloidal nature of such substances does not contribute to their properties in the sense that colloidal particles actively participate in their characteristic action. It is quite well established that in most cases the active constituents are the free molecules or ions of the surface-active material in the solution rather than aggregates of these. Certain classes of compounds are colloidal because they are surface active, and not surface active because they are colloidal.

The practical effect of the interfacial adsorption and orientation of surface-active agents may be manifested in a number of different ways. At liquid–gas interfaces the strength of the liquid film is lowered, so that it is more easily broken by mechanical influences. In such a case, the surface-

[4] G. S. Hartley, Kolloid-Z., 88, 22–40 (1939).
[4a] W. C. Preston, J. Phys. Colloid Chem., 52, 84–97 (1948).

active agent promotes foaming and suds or lather formation. At liquid–solid interfaces a similar weakening of the liquid film occurs, rendering the liquid less coherent within itself and more adherent to the solid surface. This promotes wetting of the solid, which in turn causes the liquid to spread upon the solid surface and to penetrate minute pores or openings. It is to be noted that the promotion of wetting can be reversed, by the application of suitable materials to the solid. Thus, in the treatment of fabrics for water repellency, the fibers of the fabric are coated with materials which are hydrophobic in nature and inhibit wetting to such an extent that water is unable to penetrate the fabric pores.

From the industrial standpoint a highly important case of surface action is that occurring between two immiscible liquids, as oil and water. In this case the presence of surface-active molecules at the interfaces makes the latter more readily extensible, so that upon agitation one phase may be more easily broken up into small droplets and dispersed in the other, to form an emulsion. After the emulsion is formed, orientation of the surface-active molecules at the surface of the droplet forms a protective film which prevents the droplets from coalescing upon contact with each other.

1. QUANTITATIVE RELATIONSHIPS

The operations in which surface action is important, including foaming and defoaming, wetting and dewetting, emulsification and de-emulsification, and flocculation and deflocculation, all involve the extension or restriction of liquid–liquid, liquid–solid, liquid–gas, or solid–gas interfaces. Changes in surface or interfacial area are associated with corresponding and definite changes in the free surface energies of the surfaces involved; consequently, these operations are susceptible to mathematical treatment.

Numerically, the free energy of a surface, in terms of ergs per square centimeter, is equal to the surface tension, expressed as dynes per centimeter. Theoretically, therefore, any surface-active material may be evaluated in terms of its effect on the surface tensions of the various surfaces in the system in which it is involved. It can be demonstrated upon the basis of thermodynamic reasoning that adsorption at an interface and lowering of the surface tension go hand in hand. The quantitative relationship between the amount of adsorption and the lowering of surface tension was deduced by Willard Gibbs, in the form of the so-called Gibbs adsorption equation.[5] Surface tensions of gas–liquid and liquid–liquid systems may be easily and accurately measured by a variety of methods. There are at present no methods, however, for determining surface tensions at solid–gas and solid–liquid interfaces.

[5] See N. K. Adam, *The Physics and Chemistry of Surfaces,* 3rd ed., Oxford University Press, London, 1941, pp. 178–201.

(a) Liquid–Gas Interfaces

Extension of the interface between a liquid and a gas, which occurs when a liquid is broken up into droplets or a foam, must be accompanied by an input of energy to overcome the adhesion of the liquid to itself; this energy reappears as free energy of the extended liquid surface. As indicated above, the total free energy of the surface is numerically equal to the area of the surface times the surface tension. Since division of a portion of the liquid across a plane produces *two* new surfaces, the energy or "work" of adhesion of the liquid (sometimes termed the cohesional work of the liquid) is equal to *twice* the surface tension.

(b) Liquid–Liquid Interfaces

When the interface between two immiscible liquids is extended (as it is, for example, in the formation of an emulsion), considerations apply which are entirely similar to the above, except that here the energy factor is related to the *interfacial tension* between the two phases. In general, the interfacial tension approximates the difference between the surface tensions of the two liquids,[6] or:

$$\gamma_{AB} = \gamma_A - \gamma_B \tag{1}$$

where γ_A = surface tension of liquid A, γ_B = surface tension of liquid B, and γ_{AB} = interfacial tension between A and B.

A low interfacial tension occurs when the adhesion of the two liquids is strong in relation to the internal cohesion of each separate liquid, and a high interfacial tension occurs when a converse relationship holds. If an interface is destroyed by separation of the two phases, the free surface energy of the interface is replaced by a quantity of energy equal to the sum of the surface energies of the two liquids; hence the work of adhesion in effecting this separation, W_{AB}, is given by the Dupré equation:

$$W_{AB} = \gamma_A + \gamma_B - \gamma_{AB} \tag{2}$$

(c) Liquid–Solid Interfaces

The equation for the work of adhesion at a liquid–solid interface is analogous to equation (2) above:

$$W_{SL} = \gamma_{SA} + \gamma_{LA} - \gamma_{SL} \tag{3}$$

In practice, this equation is not useful because of the impossibility of directly determining the surface tension of the solid and the interfacial

[6] G. N. Antonoff. *J. chim. phys.*, *5*, 372–385 (1907).

tension between liquid and solid. However, the liquid–solid work of adhesion can be determined indirectly, as outlined below.

(d) Boundaries between Three Phases

In dealing with the phenomena of wetting and detergency it is often necessary to consider, not simply interfaces or boundaries between two phases, but boundaries where three phases are in contact, e.g., a liquid, a solid, and a gas, or a solid and two immiscible liquids. In such cases, quantitative information is furnished by the *contact angle,* or the angle at which the liquid (or each liquid) meets the solid surface (Fig. 47). Contact angles may vary from 0°, indicating complete wetting of the solid to nearly 180°, in the case of almost complete lack of wetting, or in other words, lack of adhesion between solid and liquid.
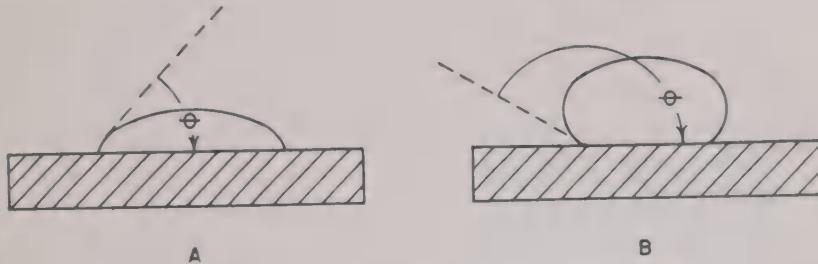
Fig. 47. Liquid droplets on a solid surface with: (A) contact angle low, and (B) contact angle high.

Contact angles are directly related to the surface tensions existing at the various interfaces in the system. The relationships between contact angles and surface tensions have been well stated by Adam,[5] from whom the following equations are taken.

For the contact angle, θ, of a liquid in contact with a solid in air:

$$\cos \theta = (\gamma_{SA} - \gamma_{SL})/\gamma_{LA} \qquad (4)$$

where γ_{SA} = interfacial tension, solid–air, γ_{SL} = interfacial tension, solid–liquid, and γ_{LA} = interfacial tension, liquid–air.

For the contact angle, θ_A, of a liquid, A, in contact with a solid and another liquid, B:

$$\cos \theta_A = (\gamma_{BS} - \gamma_{AS})/\gamma_{AB} \qquad (5)$$

where γ_{BS} = interfacial tension, liquid B–solid, γ_{AS} = interfacial tension, liquid A–solid, and γ_{AB} = interfacial tension, liquid A–liquid B. The contact angle, θ_B, of liquid B, is, of course, the supplement of θ_A.

Since surface tensions at liquid–solid and gas–solid interfaces are not measurable, certain other expressions avoiding these expressions are more

useful than equations (4) and (5). The work of adhesion, W_{SL}, between a liquid and a solid in air is defined by equation (3). In the case of two liquids, A and B, in contact with a solid, the works of adhesion W_{SA} and W_{SB} between the solid, and liquids A and B, respectively, are as follows:

$$W_{SA} = \gamma_A + \gamma_S - \gamma_{AS} \tag{6}$$

$$W_{SB} = \gamma_B + \gamma_S - \gamma_{BS} \tag{7}$$

Combining (3) and (4):

$$\cos \theta = \frac{W_{SL} - \gamma_{LA}}{\gamma_{LA}} \tag{8}$$

Combining (5), (6), and (7):

$$\cos \theta_{AB} = \frac{(W_{AS} - \gamma_A) - (W_{BS} - \gamma_B)}{\gamma_{AB}} \tag{9}$$

The quantities, $W_{AS} - \gamma_A$, $W_{BS} - \gamma_B$, and $W_{SL} - \gamma_{LA}$ are referred to as "adhesion tensions." They are a measure of the adhesion of the liquid for the solid minus the cohesion of the liquid, or in other words, of the tendency of the liquid to wet the solid.

2. FOAMING AND DEFOAMING

The formation of froth or foam on a liquid is accompanied by a tremendous extension of the liquid–air interface. Consequently, foaming will be favored by the presence of any substance in the liquid which lowers the surface tension of the latter and decreases the work which must be done to increase the interface.

Closely related to the readiness with which a liquid foams is the matter of stability of the foam. Since the surface tension of the liquid tends constantly to diminish the surface, a low surface tension likewise contributes toward foam stability.

It has been well established, however, that the surface tension of a liquid is not the decisive factor in determining whether it shall foam readily and produce a foam which is stable. The effectiveness of certain surface-active materials in promoting and stabilizing foams appears to be due to their tendency to concentrate in the interface, and to their peculiar properties in concentrated surface films, rather than to their effect on the surface tension *per se*.

Foulk,[7] in an investigation of foaming in solutions of organic compounds,

[7] C. W. Foulk, *Ind. Eng. Chem.*, *21*, 815–817 (1929). C. W. Foulk and J. N. Miller. *ibid.*, *23*, 1283–1288 (1931).

found that stable foams were formed only when there was an appreciable difference between the static and dynamic surface tensions of the solution, or in other words, when there was a tendency of the dissolved substance to concentrate at the liquid–air interface. Pure liquids are incapable of foaming. Liquid films (of foams) are formed, according to Foulk's concept, by the near approach to each other of two liquid surfaces already formed. A concentration gradient of dissolved substance in the film is considered essential to prevent the two surfaces from approaching to the point of coalescence.

Adam,[1] in discussing the stability of foams, has emphasized the necessity of a stable film being able to vary easily and quickly in surface tension, both in order to meet permanent differences of stress in its different parts, and to absorb local mechanical shocks. In this connection it is significant that most solutions of foam-inducing substances (particularly those of low or medium molecular weight) exhibit their maximum foam-producing capacities, not at concentrations at which surface tension is at a minimum, but rather at lower concentrations, where variation in concentration has a large effect on surface tension.

There is evidence that some surface films, particularly those of the higher fatty acid soaps, actually exhibit plastic properties, due to the close packing of large molecules (Freundlich[1] and Wilson and Ries[8]). That such films would produce highly stable foams is obvious. Adam considers that the speed with which surface-active molecules can diffuse from the surface to the interior, and *vice versa*, is probably important in determining the stability of the film. He attributes the extreme persistence of concentrated soap foams to the probable slow diffusion of the large soap molecules. It is noteworthy that in some instances, as for example in a solution of commercial lecithin in a fat or oil, the dissolved substance may contribute strongly to foaming without marked effect on the surface tension of the liquid.

Synergistic effects have been noted in the use of foaming agents; according to Merrill and Moffett,[8a] soaps prepared from natural fats and oils produced more stable foams than the soaps of any of the corresponding single fatty acids.

In commercial practice it is more often necessary to destroy undesirable foams than to promote foam formation. The effective defoaming or foam-breaking agents are liquids which are immiscible with the primary liquid and have great spreading power thereon, so that a relatively small quantity will form a thin continuous coating film. In a sense, they do not function as foam breakers through surface activity, but through a covering action which is more nearly mechanical in nature. However, their

[8] R. E. Wilson and E. D. Ries, *First Colloid Symposium Monograph*. Univ. of Wisconsin, Madison, 1923, pp. 145–170.
[8a] R. C. Merrill and F. T. Moffett, *Oil & Soap*, *21*, 170–175 (1944).

surface properties in relation to the primary liquid are important in determining their very essential spreading ability.[8b]

3. EMULSIFICATION

An emulsion is usually defined as a system of two immiscible liquids, one of which is dispersed in the other in the form of small droplets. This definition must be broadened somewhat to include all of the systems which are commonly referred to as emulsions in industrial practice. Virtually all industrially important emulsions consist of water or an aqueous solution and a fatty or hydrocarbon oil. In oil and fat technology, particular attention must be given to emulsions in which one phase is a fat (which is a plastic solid), rather than a liquid oil. Thus, for example, butter and margarine consist of a dispersed phase of watery droplets enclosed in a continuous phase of plastic fat. A cake dough, on the other hand, consists of a watery continuous phase surrounding a dispersed phase of plastic fat particles. In a true water–oil emulsion the small dispersed particles are constricted to a spherical form by the forces of surface tension. The fat particles in the dough, however, are not readily deformed, being plastic rather than liquid. Consequently, they are of irregular rather than globular shape.

All the surface-active materials which are effective as emulsifying agents markedly lower the interfacial tension between the two liquid phases. Since the interface must be very greatly extended in producing an emulsion, the energy considerations mentioned previously in connection with foams apply equally to the formation and the stability of emulsions. In other words, lowering of the interfacial tension is in itself favorable to both the production of emulsions and their stabilization.

While a low interfacial tension is undoubtedly an important factor in the production of a stable emulsion, it is by no means the only factor involved. It is well recognized that the utility of an emulsifying agent in specific industrial applications cannot always be predicted simply from measurements of the degree to which this agent lowers the interfacial tension of the liquids in question. Its effectiveness will be determined also by such considerations as the size and motility of the surface-active molecules, and the degree to which they exhibit plasticity or rigidity in closely packed layers in the interfacial film.

The phenomenon of emulsification is rendered somewhat more complicated than that of foam formation by the existence of two liquid phases. An emulsion of liquids A and B may consist of a dispersion of A in B or of B in A. At first thought it might appear that the volume relationship

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[8b] For recent discussion of foam inhibitors and the theory of foam inhibition, see S. Ross and J. W. McBain, *Ind. Eng. Chem.*, *36*, 570–573 (1944); J. V. Robinson and W. W. Woods, *J. Soc. Chem. Ind.*, *67*, 361–365 (1948); S. Ross, *Chem. Inds.*, *64*, 757–759 (1949).

between the two liquids would determine the type of emulsion, *i.e.*, the liquid present in the lesser quantity would tend to become the disperse phase. This, however, is not necessarily the case. In some instances there is a tendency for the emulsion to break or to invert from one type to another if an attempt is made to increase the relative volume of the disperse phase beyond a certain point. However, in many important emulsions, *e.g.*, in mayonnaise, the volume of the disperse phase greatly exceeds that of the continuous phase. It is readily possible to prepare stable emulsions in which the volume of the inner phase exceeds that obtaining in spherical close packing, and in which the globules of this phase are consequently deformed, if an emulsifying agent is used which markedly resists coalescence of the globules. Actually, the question of which liquid shall be dispersed is determined by surface tension considerations which are definitely related to the nature of the emulsifying agent.

The most commonly accepted theory relating to emulsion type was deduced by Bancroft and co-workers[9] and has been confirmed by the work of Clowes[10] and others. According to this theory, the film of oriented surface-active molecules between the two phases of the emulsion is conceived to be in effect a third phase, possessing separate surface tensions against each of the two liquids which form the emulsion. In the case of a water–oil emulsion, if the film has a greater affinity for water than for oil, its surface tension will be lower on the water than on the oil side. The film surface will then tend to curve in such a direction as to reduce the total surface tension, *i.e.*, it will form a curve with the area of low surface tension on the outside and that of high surface tension on the inside, or will tend to enclose globules of oil in water. If the film has a greater affinity for oil than for water, the effect will be reversed, and the tendency will be to form an emulsion of water in oil.

In general, surface-active agents which are freely soluble in water but sparingly soluble in oil will form emulsions of the oil-in-water type, whereas those more soluble in oil than in water will form emulsions of the water-in-oil type. Thus sodium and potassium soaps stabilize oil-in-water emulsions; soaps of calcium or magnesium stabilize emulsions of the opposite type.

The influence of the emulsifying agent upon the emulsion type is not absolute. In some cases it is possible to produce an emulsion of one type by one method of mixing and of a reverse type by a different mixing procedure. In other cases, as for example in the preparation of a cake dough, the emulsion may invert from one type to another during its preparation. In a number of important processes involving emulsions, *e.g.*, in the churning of butter, a phase inversion is an essential part of the process.

[9] W. D. Bancroft, *J. Phys. Chem.*, *17*, 501–520 (1913); *19*, 275–309 (1915). W. D. Bancroft and C. W. Tucker, *ibid.*, *31*, 1681–1692 (1927).
[10] G. H. A. Clowes, *J. Phys. Chem.*, *20*, 407–450 (1916).

It may be said, however, that with a given system of liquids and a single stable emulsifying agent there is practically always one type of emulsion which is much more stable than the other. In most cases of phase inversion it can be demonstrated that inversion is accompanied by treatment which either alters the chemical constitution of the emulsifying agent or introduces a second surface-active agent.

In a number of cases it has been found that a combination of two emulsifying agents—one of which is water-soluble and the other oil-soluble—will yield more stable oil-in-water emulsions than a single surface-active agent of either type. It may be presumed that the two agents interpenetrate at the interface, to form a film of greater thickness and higher strength and plasticity than the film produced by a single molecular species. On the other hand, the stability of a water-in-oil emulsion is usually lessened by the addition of a second water-soluble emulsifying agent. In fact, a common technique for breaking emulsions of this type involves the use of a water-soluble agent, to neutralize the effect of the oil-soluble material originally responsible for the emulsion. Antagonism may exist between two natural emulsifying agents in the same material, *e.g.*, between the lecithin and cholesterol present in eggs.

Finely divided solid materials tend to collect at interfaces and stabilize emulsions. Contrary to popular belief, the most stable emulsions are not necessarily those in which the internal phase is dispersed to the greatest possible degree, as extreme extension of the interface may lead to impoverishment of the surface-active agent therein.

4. WETTING OF SOLIDS

The relationship between the surface tensions of a liquid–solid system and the degree to which the liquid wets the solid have been stated previously, in equations (1) to (9). It is only necessary to add here that any substance is surface active in such a system if its presence alters the degree to which wetting occurs.

So-called "wetting agents" are the most common liquid–solid surface-active materials. These consist of water-soluble compounds which are oriented at the surface with the polar heads of the molecules in the water phase and the nonpolar tails toward the solid. There are other surface-active compounds, however, such as the "collectors" used in ore flotation, whose polar groups are more strongly attracted toward the solid than the liquid. Molecules of these compounds assume a reverse orientation at the surface of the solid, and hence decrease the degree to which it is wetted.

There are a number of different ways in which surface-active agents may alter the characteristics of a liquid–solid system. In many applications the function of the surface-active agent is merely to promote the spread-

ing of a liquid upon a more or less smooth solid surface, so that the latter may be easily coated with a uniform and adherent liquid film. In some cases, as in the use of wetting agents in adhesives, the surface-active agent contributes to the strength of the bond between the solid and the liquid. In many such instances the liquid is later converted to a solid, so that in effect the wetting agent assists in establishing a bond between two solids.

Surface-active agents are often important in their effect upon the ease with which a liquid penetrates a mass of fibers, or other porous structure in which capillarity comes strongly into play. The driving force which impels a liquid to penetrate a capillary space in a solid material may be expressed by the following equation:

$$F = \gamma_{LA} \cos \theta \, x \qquad (10)$$

where F is the force in question, γ_{LA} is the surface tension of the liquid against air, θ is the contact angle of the liquid against the solid, and x is a factor determined by the size of the capillary. Wetting agents increase the value of F in the above expression by decreasing the contact angle of the liquid against the solid. Dewetting or water-proofing agents decrease the value of F or even cause it to assume a negative value, by increasing the contact angle.

Powney,[11] in discussing the penetration of fabrics, has pointed out that the entry of a liquid into very small interstices will be followed by a local impoverishment of its content of surface-active molecules, from the relatively great amount of adsorption of the latter on the solid surfaces. In the later stages of penetration, therefore, the rate at which diffusion can take place to replenish this impoverishment is important.

5. Miscellaneous Effects of Adsorption on Solid Surfaces

Because of the high interfacial tension of most solids against water or other liquids, solid particles suspended in a liquid generally tend to reduce their effective surface through flocculation. The effectiveness of filtration as a means of separating solids from liquids depends to a large degree upon a similar phenomenon, inasmuch as filters will commonly retain solid particles of smaller dimensions then their actual pore size. Surface-active agents tend to cause deflocculation, or act as "peptizing agents" or "protective colloids" through their ability to reduce the interfacial tension. In addition, it is probable[12] that certain agents function simply through their ability to form relatively thick adsorbed layers upon the

[11] J. Powney, in International Society of Leather Trades' Chemists, British Section, *Wetting and Detergency* 2nd ed., Chemical Pub. Co., New York, 1939, pp. 185–196.
[12] A. de Waele, in International Society of Leather Trades' Chemists, British Section, *Wetting and Detergency*. 2nd ed., Chemical Pub. Co., New York, 1939, pp. 57–66.

surface of the solid particles. Such layers serve to maintain contiguous particles at a sufficient distance to avoid the influence of mutually attractive surface forces. Most of the materials which are effective deflocculators contain molecules of relatively large weight and complicated structure. Examples of such materials are phosphatides, and oxidized and polymerized glycerides.

Surface-active agents of the above class not only maintain paint pigments and similar materials in a high degree of dispersion,[13] but may also markedly influence the plasticity or viscosity of suspensions to which they are added. The latter effect is fully explainable upon the basis of their influence upon adhesional forces between the solid particles. An outstanding example of this phase of surface action is furnished by the use of lecithin to reduce the consistency of chocolate–sugar compositions.

An important industrial use of surface-active agents (particularly in the dyeing of textiles) is to modify the particle size of precipitates, *i.e.*, to insure the deposition of fine and well-dispersed crystals from solution. In systems where supercooling is marked, as in fats or oils, the adsorption of surface-active materials on submicroscopic crystal nuclei may have a marked inhibitory effect upon crystallization.

The inhibitory effect of low concentrations of certain substances upon crystal formation and growth appears to be explainable upon the basis of preferential adsorption of surface-active molecules on the crystal faces. The efficacy of lecithin in preventing "bloom" on chocolate surfaces is due to its dispersive effect upon fat crystals. Lecithin is also an effective crystallization inhibitor in winterized cottonseed oil. Oxidized, polymerized oils and fatty acid esters of sorbitol or other higher alcohols have also been used as crystallization inhibitors (see Chapter VII).

6. DETERGENCY

The mechanism by which soap and other detergents clean is manifestly complex, and different authorities are by no means in agreement concerning its details. However, the principles discussed in the following paragraphs appear to be more or less generally accepted by modern workers in this field, and cover the more important phases of detergent action.

In a great many soiled surfaces, the "dirt" is bound to the surface by a thin film of oil or grease. The cleaning of such surfaces involves the displacement of this film by the detergent solution, which is in turn washed away by rinse waters.

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[13] For an excellent review of wetting, with particular attention to paint pigments, and extensive literature references, see A. O. Allen, A. Knoll, L. W. Ryan, and C. A. Murray, Chapter I in *Protective and Decorative Coatings*, Vol. IV, J. J. Mattiello, ed., Wiley, New York, 1944. See also E. K. Fischer and D. M. Gans, Chapter 14 in *Colloid Chemistry*, Vol. VI, J. Alexander, ed., Reinhold, New York, 1946.

The mechanism by which this displacement occurs has been subjected to mathematical analysis by Adam, and the results reported by Robinson.[14] It has been demonstrated that the oil film breaks and separates into individual droplets under the influence of the detergent solution. In other words, the contact angle of the oil with the solid surface is caused to change from approximately 0° to 180°. The oil droplets are, of course, detached from the surface with relative ease by mechanical action.[15]

As an expression of the relationship between the above mentioned contact angle, the surface tension and the adhesion tension (a.t.) in the system, the following equation is presented:

$$\cos \theta_{AB} = \frac{\text{(solution–solid a.t.)} - \text{(oil–solid a.t.)}}{\text{oil–solution interfacial tension}} \qquad (11)$$

This equation is simply equation (9), restated in semimathematical terms. It is to be noted that the angle θ_{AB} in this equation is that made by the oil–solution interface *in the solution*. It is, therefore, the supplement of the contact angle of the oil. In the process of displacement mentioned above it must change from approximately 180° to 0°.

When $\theta_{AB} = 0$, the value of $\cos \theta_{AB}$ is 1. At higher values of θ_{AB}, $\cos \theta_{AB}$ is less than 1, or is a negative quantity. Therefore, for detergent action to be most efficient, the expression on the right hand side of equation (11) should be as large as possible. Detergents contribute to a large value both by increasing the adhesion tension between the solid and the aqueous phase and decreasing the interfacial tension between the aqueous and oily phases.

Nonoily dirt is probably removed by a more or less analogous process, *i.e.*, it is displaced and carried away by the detergent solution through the superior affinity of the latter for the solid surface. It has been frequently observed, however, that dirt of any kind is much more difficult to remove from fabrics, etc., in the absence of oil or grease.

Emulsification and deflocculation undoubtedly play a considerable part in detergent action. Obviously, if detached oil droplets and dirt particles did not become suspended in the detergent solution in a stable and highly dispersed condition, they would be inclined to flocculate or coalesce into aggregates large enough to be redeposited on the cleansed surface. In the washing of fabrics and similar materials, small oil droplets or fine, deflocculated dirt particles are more easily carried through interstices in the

[14] C. Robinson, in International Society of Leather Trades' Chemists, British Section, *Wetting and Detergency*. 2nd ed., Chemical Pub. Co., New York, 1939, pp. 137–151.

[15] For photomicrographs illustrating this action, see reference 14, and also the photographs of W. Kling, E. Langer, and I. Haussner, *Melliand Textilber.*, 25, 198–202 (1945), which are reproduced by Schwartz and Perry (footnote 1), pp. 364–367. See also C. Robinson in *Wetting and Detergency* (footnote 1), pp. 137–151.

material than are relatively large ones. The protective colloid action of
the detergent is also important in this connection, in preventing retention
of detached dirt by the fabric. It will be recalled that the manner in which
soap enables carbon black suspensions to pass through filter paper con-
stitutes one of the classic illustrations of the action of a protective colloid.

McBain,[16] among others, has emphasized the possible role of ion
exchange in removing dirt which is derived from an ionizable material.
The exchange involved is represented as follows:

$$\text{fabric–dirt} + \text{soap} = \text{fabric–soap} + \text{dirt–soap}$$
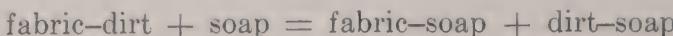
After washing, fabrics invariably retain a considerable amount of strongly
adsorbed soap.[17] The washing operation is not an irreversible process,
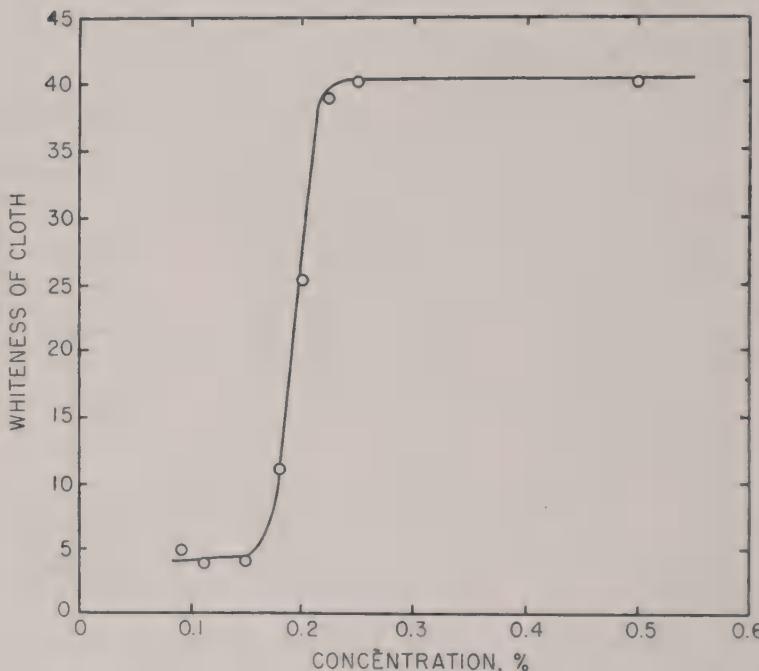
Fig. 48.   Detergency curve for sodium myristate at 71°C. Whiteness of stand-
ard soiled and washed cotton muslin *vs.* concentration of detergent.[4a]

but one in which equilibrium is eventually attained between dirt adsorbed
(in small amount) on the fabric and dirt suspended in the washing bath
or solution. Hence, when clean and soiled fabrics are washed together,
they tend to come out of the bath equally clean (or soiled), through re-
distribution of the dirt carried by the soiled members.[18]

McBain[16] has also suggested that solubilization (see page 360) is also

[16] James W. McBain, in *Advances in Colloid Science*, Vol. I. Edited by E. O.
Kraemer. Interscience. New York. 1942, pp. 99–142.
[17] K. W. Gardiner and L. B. Smith, *J. Am. Oil Chem. Soc.*, 26, 194–196 (1949).
[18] F. H. Rhodes and S. W. Brainerd, *Ind. Eng. Chem.*, 21, 60–68 (1929).

a major factor in detergency. Hartley[19] does not consider that the solvent action of detergents is important in washing operations conducted in solutions of ordinary detergent concentration. However, he admits the probability of it being a major factor in such operations as washing the hands, in which the detergent is applied in a concentrated form. In the washing of fabrics, Preston[4a] has pointed out that the detergency of a given sodium soap or sodium alkyl sulfate rises to a maximum at a relatively low concentration of the surface-active agent, after which it is increased little or not at all by the addition of further amounts of the agent (Fig. 48). As the end of the sharply rising portion of the curve corresponds to the point at which fatty anions in the solution attain a maximum concentration, but is far short of the point at which large colloidal micelles appear in quantity, this would appear to relegate solubilization to a minor role in ordinary washing processes.

A point to be particularly emphasized is that, contrary to a popular impression, there is no necessary relationship between the efficiency of a detergent and its ability to form foam or suds, although it is possible that foaming contributes something to detergency through a mechanical effect.[20] In special cases, as in the use of shaving soaps, the detergent must form a foam or lather for the detergent solution to be efficiently applied.

In practice, a washing solution does not often consist simply of a detergent dissolved in pure water. Natural waters contain varying amounts of mineral salts and the solution may also contain other electrolytes, either through accident or design. The presence of electrolytes may greatly influence the action of the detergent.

The reaction of ordinary soaps with hard waters containing soluble calcium and magnesium salts is a matter of common experience. It not only produces insoluble curds of calcium and magnesium soaps, which are difficult to remove from fabrics, but also makes the consumption of soap excessive. In very hard waters large quantities of soap are required to precipitate these compounds before there is any soap available for detergent action. However, most of the synthetic detergents, such as the sodium alkyl sulfates and the Igepons, do not form insoluble compounds with hard waters. In soap products so-called "builders," such as sodium silicate, soda ash, or tetrasodium pyrophosphate, are often incorporated to serve as water softeners and decrease the amount of soap consumed in softening the water. These materials also assist in neutralizing the natural acidity of soiled clothing, and serve as buffering agents to maintain soap solutions at the proper pH for most effective action (about 10.5–11.0 for

[19] G. S. Hartley, in International Society of Leather Trades' Chemists, British Section, *Wetting and Detergency*. 2nd ed., Chemical Pub. Co., New York, 1939, pp. 153–162.
[20] J. Sisley, *Corps Gras Savons*, *1*, 66 (1943).

laundering operations).[21]   Many of the complex sodium phosphates and silicates improve the detergency of soaps through their action as defloc-culating agents.[22]   In addition, the presence of electrolytes may have a considerable effect on the surface tension of solutions of soaps as well as other detergents (page 363). Sodium tripolyphosphate is particularly effective in improving the detergency of certain synthetic surface-active agents, e.g., sodium alkyl sulfates.

The detersive action of soaps and synthetic detergents may also be improved through the presence of certain organic materials which act as protective colloids (page 330). Although numerous instances of synergism in detergents have been reported,[23] the significance of such effects appears to be generally discounted by detergent manufacturers at present, and the products now on the market consist generally of a single surface-active material, rather than a mixture. In particular, mixtures of soap with so-dium alkyl sulfates or other common synthetics do not appear promising, even though such products were manufactured in considerable quantity during the last World War for military use as salt-water soaps.

There are definite limitations to the range of pH within which certain detergents will function. Ordinary soap solution will decompose at a pH below about 10, hence must necessarily be alkaline. Most of the nonsoap detergents are effective in neutral solution. The so-called cation-active detergents, in which the major part of the molecule is positively charged, may be used in acid solution.

It may be mentioned, finally, that the nature of the surface to be cleaned has some influence upon the relative effectiveness of different de-tergents. This follows from the fact that one of the determining factors in detergent action is the affinity of the detergent solution for the soiled sur-face, which depends in turn upon the chemical nature of the surface as well as the detergent. Thus, for example, the nonsoap detergents are relatively efficient, in comparison with soaps, in washing woolen fabrics or silks, but somewhat less efficient for washing cotton or rayon.

C. Physical Chemistry of Soaps and Related Materials

1. Phase Behavior of Aqueous Systems

The sodium and potassium soaps of the common fatty acids are capable of existence in a remarkable variety of forms. The soap–water phases represented by niger, neat soap, and soap curd have been recognized since the beginnings of the soap-boiling art. However, knowledge of the true

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[21] F. D. Snell, Ind. Eng. Chem., 25, 1240–1246 (1933).
[22] See, for example, J. Powney and R. W. Noad, J. Textile Inst., 30, 157–171T (1939).
[23] See, for example, F. D. Snell, J. Am. Oil Chem. Soc., 26, 338–341 (1949).

ature of these and other aqueous soap phases dates from the work of Maclennan,[24] which was reported in 1923.

By the microscopic examination of samples with the aid of polarized light, Maclennan demonstrated that neat soap belongs to the class of anisotropic or crystalline liquids, that niger is an ordinary isotropic solution, devoid of crystalline structure, and that soap curd and ordinary finished soap consist of a heterogeneous mass of solid, fibrous crystals enmeshing a liquid phase. Thus he established the existence of three distinct phases: isotropic soap solution, neat soap, and curd fibers. Later, McBain and Langdon[25] distinguished a "middle soap." According to Void et al.[25] this is not a liquid crystalline form, but consists, in spite of its stiff consistency, simply of soap micelles in water. More recently, Vold[26] has produced evidence of a liquid crystalline phase, "superneat soap," and McBain and co-workers[27] have detected a new waxlike phase which they have termed "kettle wax."

Anhydrous or nearly anhydrous soaps exhibit an even greater variety of forms. The researches of Ferguson and associates,[28] later extended by Vold and co-workers,[29] have revealed that a single pure anhydrous soap may pass through at least seven successive phases as it is heated from ordinary room temperature to the point where it becomes a completely isotropic liquid.[30] In the case of sodium palmitate the different forms are: curd fiber, to 117°C.; subwaxy, to 135°; waxy, to 172°; superwaxy, to 208°; subneat, to 253°; neat, to 295°; and isotropic liquid, above 295°. The term "neat soap" refers here simply to the form which first appears upon cooling the isotropic liquid, and has no necessary identity with "soap boiler's neat soap." There is some evidence that there may be other phases, as yet undefined, within the lower range of temperatures.

While it is evident from calorimetric and dilatometric examination that the preceding seven forms are distinct phases, connected by first-order transitions, x-ray examination fails to distinguish between the three waxy forms as a group and the two neat forms as a group.[31]

The change from one phase to another contiguous phase is in every

[24] K. Maclennan, *J. Soc. Chem. Ind.*, *42*, 393–401T (1923).
[25] J. W. McBain and G. M. Langdon. *J. Chem. Soc.*, *127*, 852–870 (1925). T. M. Doscher and R. D. Vold. *J. Phys. Colloid Chem.*, *52*, 97–109 (1948).
[26] R. D. Vold, *Soap, 16*, No. 6, 27–30 (1940).
[27] J. W. McBain, R. C. Thorburn, and C. G. McGee, *Oil & Soap, 21*, 227–230 (1944); J. W. McBain, K. Gardiner, and R. D. Vold, *Ind. Eng. Chem.*, *36*, 808–810 (1944).
[28] R. H. Ferguson, R. D. Vold, and F. B. Rosevear, *Oil & Soap, 16*, 48–51 (1939).
[29] M. J. Vold, M. Macomber, and R. D. Vold, *J. Am. Chem. Soc.*, *63*, 168–175 (1941). R. D. Vold and M. J. Vold, *J. Am. Chem. Soc.*, *61*, 808–816 (1939).
[30] Apparently the soaps of potassium, lithium, cesium, and rubidium undergo a similar though not identical series of transitions. See R. D. Vold and M. J. Vold, *J. Phys. Chem.*, *49*, 32–42 (1945).
[31] H. Nordsieck, F. B. Rosevear, and R. H. Ferguson, *J. Chem. Phys.*, *16*, 175–180 (1948).

case reversible. Furthermore, in the regions with which the soap boiler is concerned, there is no significant fractionation of the many chemical individuals in commercial soaps as these soaps undergo transition from one phase to another; in other words, with respect to phase behavior, a commercial soap behaves essentially like a soap of a single fatty acid.[25,32-34] Consequently, as first suggested by Merklen,[35] and subsequently demonstrated by McBain,[36] commercial soap–water systems are in every way amenable to Gibb's phase rule. The application of phase diagrams has been a paramount influence in establishing soap boiling— once purely an art—on a scientific basis.
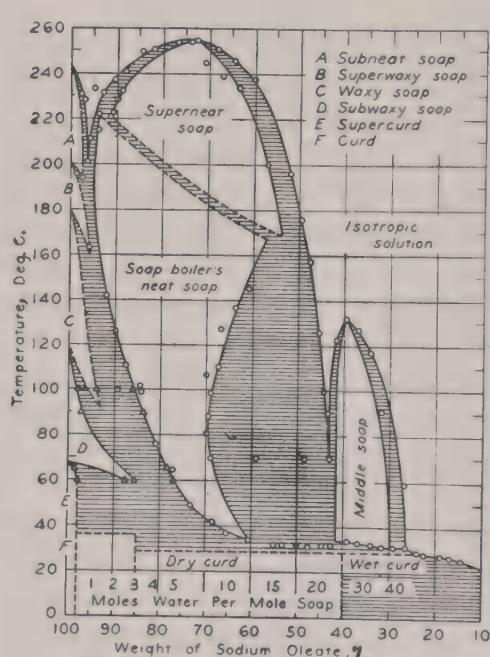
Fig. 49. Phase diagram of the system sodium oleate–water.[36]
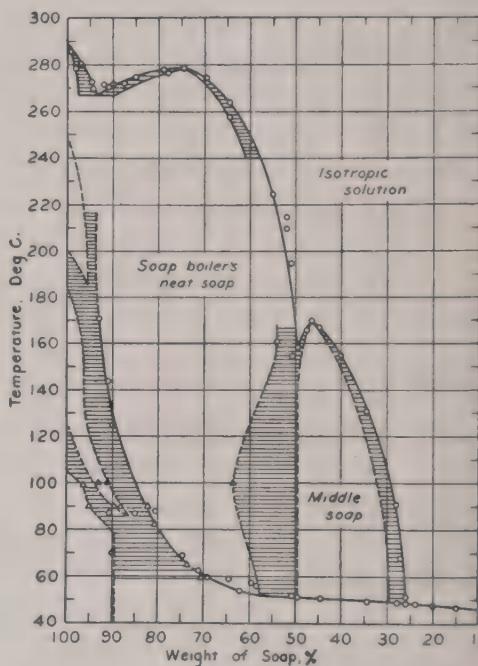
Fig. 50. Phase diagram of a commercial toilet soap and water.[36]

Phase diagrams for aqueous systems of sodium laurate, sodium myristate, sodium palmitate, sodium stearate, sodium oleate, and a commercial toilet soap have been constructed over a period of years by McBain and his associates. A revised set of diagrams for all of these systems was prepared from the best available data and presented by McBain and Lee.[36] Their diagrams for sodium oleate and commercial

[32] R. H. Ferguson and A. S. Richardson, *Ind. Eng. Chem.*, *24*, 1329–1336 (1932).
[33] R. H. Ferguson, *Oil & Soap*, *9*, 5–8, 25 (1932).
[34] J. W. McBain, M. J. Vold, and J. L. Porter, *Ind. Eng. Chem.*, *33*, 1049–1055 (1941).
[35] F. Merklen, *Études sur la Constitution des Savons du Commerce*, Marseilles, 1906. German edition by F. Goldschmidt, Halle-a.S., 1907.
[36] J. W. McBain and W. W. Lee, *Oil & Soap*, *20*, 17–25 (1943).

soap are reproduced in Figures 49 and 50. It is to be noted·that these diagrams are in some regions incomplete. In other regions the boundaries have been only tentatively placed, and hence are indicated by dotted rather than continuous lines. The typical behavior of aqueous soap systems may be deduced from the diagrams.

The two diagrams are divided into areas within which soap–water exists as a single phase, and other areas in which two contiguous phases are present in an equilibrium mixture. Tie lines drawn across the latter areas are necessarily horizontal, since they represent equilibria under isothermal conditions. The tie lines, which are drawn in the diagrams at regular intervals, give the areas of heterogeneity a shaded appearance, whereas the areas within which there is a single phase are unshaded.

In Figure 49 the transition points of the various anhydrous phases of sodium oleate are indicated along the left vertical axis of the diagram. Sodium oleate appears to differ from corresponding soaps of the saturated fatty acids in exhibiting no anhydrous neat phase. However, the curd, subwaxy, waxy, superwaxy, and subneat forms can be distinguished, as well as the isotropic phase. With the addition of a small percentage of water the anhydrous phases are brought a short distance within the hydrous region, in the form of "tongues" which are inclined sharply downward. Thus the presence of even a very small amount of water serves to lower markedly the transition points of the various anhydrous phases. With the further addition of water the anhydrous phases soon disappear and the distinctive aqueous phases make their appearance. In Figure 50 it will be noted that the transition from one anhydrous phase to another is not abrupt, but occurs over a range of temperatures. Thus, in the case of commercial soaps there is in these phases some fractionation of the various individual components during transition.

By following the 100°C. isotherm across Figure 49 from right to left it will be seen that sodium oleate assumes the following successive forms as its concentration in water at this temperature is increased from 0 to 100%: 0–31%, isotropic solution; 31–34%, isotropic solution and middle soap; 34–42%, middle soap; 42–43%, middle soap and isotropic solution; 43–44%, isotropic solution; 44–69%, isotropic solution and soap boiler's neat soap; 69–86%, soap boiler's neat soap; 86–94%, soap boiler's neat soap and waxy soap; 94–96%, waxy soap; 96–98%, waxy and subwaxy soap; 98–100%, subwaxy soap.

Similarly, the toilet soap (Fig. 50) at 100°C. is in the form of an isotropic solution from 0 to 29% concentration; between 29 and 32% it is heterogeneous and consists of isotropic solution and middle soap; from 32 to 49% it consists solely of middle soap; from 49 to 64% it is again heterogeneous, consisting of middle soap and soap boiler's neat soap; from 64 to 85% it consists entirely of soap boiler's neat soap, etc.

In a similar manner it is possible to trace the composition of a soap of given concentration as its temperature is varied. If, for example, a line representing 65% soap is traced vertically from the bottom to the top of Figure 49, it will be seen that a sodium oleate soap of this composition assumes the following forms as it is heated from ordinary room temperature to complete melting: to 32°C., curd fiber and isotropic liquid; 32–34°, curd fiber and middle soap; 34–36°, curd fiber and soap boiler's neat soap; 36–54°, soap boiler's neat soap; 54–70°, soap boiler's neat soap and middle soap; 70–130°, neat soap and isotropic solution; 130–175°, soap boiler's neat soap; 175–180°, soap boiler's neat soap and superneat soap; 180–240°, superneat soap; 240–249°, superneat soap and isotropic solution; above 249°, isotropic solution.

The various soap phases differ somewhat in consistency and gross appearance. In the case of sodium palmitate, the anhydrous phases have been described by Vold[26] as follows: curd fiber phase, a hard, opaque white solid; subwaxy phase, slightly less opaque and less hard than the curd fiber phase; waxy and superwaxy phases, similar in appearance to subwaxy, but progressively softer; subneat phase, translucent and much less viscous than the waxy phases, flowing under its own weight; neat phase, similar to the subneat phase, but less chalky; isotropic liquid, clear and relatively low in viscosity, permitting entrained air bubbles to escape readily.

The aqueous phases of sodium oleate are described by the same author as follows: middle soap, nearly transparent and very stiff, does not flow in 12-mm. tubes; soap boiler's neat soap, rather turbid and translucent, fairly fluid; superneat soap, very similar to soap boiler's neat soap, perhaps slightly clearer. The anhydrous phases are very little changed in appearance as they are extended into the hydrous region. Isotropic soap solution is, of course, relatively clear and fluid.

For data on the phase behavior of potassium soaps of certain fatty acids, reference may be made to the publication of McBain and Sierichs.[37] The effect of common soap builders and other electrolytes on commercial soap–water systems has been outlined by Merrill.[38] A limited amount of information is available on systems of water and rosin soaps, with and without electrolyte present,[39] and on amine soaps.[40]

Information on the effect of common salt on soap–water systems may be found in Chapter XX.

At ordinary atmospheric temperatures sodium soaps of high moisture content consist of a heterogeneous mixture of curd fibers with isotropic liquid. Water is associated in small amount with the solid crystals, but

[37] J. W. McBain and W. C. Sierichs, *J. Am. Oil Chem. Soc.*, *25*, 221–225 (1948).
[38] R. C. Merrill, *Ind. Eng. Chem.*, *39*, 158–166 (1947); *J. Am. Oil Chem. Soc.*, *25*, 84–95 (1948).
[39] R. C. Merrill and R. Getty, *J. Phys. Colloid Chem.*, *52*, 167–179 (1948).
[40] E. Gonick and J. W. McBain, *J. Am. Chem. Soc.*, *68*, 683–685 (1946).

at present it is controversial as to whether such water forms definite hydrates.[43]

The point T_S, at the lower left corner of the field of isotropic solution, known as the "Krafft point" is significant in that here the boundary between isotropic solution and curd fiber isotropic solution is nearly horizontal and a slight change in the temperature is accompanied by a very large change in solubility. In the case of the commercial soap, for example (Fig. 50), this temperature is 59°C. At this temperature the solubility of the soap (as ordinary isotropic solution) is about 26%; at 45° its solubility is about 2%.

The values listed by McBain and Lee[36] for T_S of the various soaps, as well as certain other important values derived from the phase diagrams, are given in Table 85. The solubility of a soap is, of course, determined by the position of the boundary of the isotropic solution area extending to the right and downward from T_S (Fig. 51). For information on the solubility of soap (sodium palmitate) in various organic solvents, reference may be made to the publications of Leggett and co-workers[41] and Bondi.[42]

TABLE 85

SOME IMPORTANT VALUES FOR FIVE PURE SOAPS AND A COMMERCIAL SOAP[a]

Soap	Temp. of ready solubility, (T_S), °C.	Lowest temp. for 70% neat, °C.	Lowest temp. for neat, °C.	Lowest concn. for neat, per cent soap	Left boundary for neat at 100°C., per cent soap
Sodium laurate	42	76	62	58	80
Sodium myristate	60	84	70	51	79
Sodium palmitate	71	88	80	63	78
Sodium stearate	77	91	83	50	79
Sodium oleate	32	43	34	61	86
Toilet soap	49	60	51	58	85
Most commercial soaps	45–55	—	—	—	—

[a] According to J. W. McBain and W. W. Lee, *Oil & Soap*, *20*, 17–25 (1943).

The phase diagrams as outlined apply, of course, only to systems which are in equilibrium. Supercooling cannot take place in the transition of one liquid phase to another, as for example, in the transition between isotropic liquid and middle or neat soap. However, in the case of transition from neat or middle soap to curd fiber, as in any other crystallization from a viscous liquid, there may be marked supercooling. Thus Laing and

[41] C. W. Leggett, Jr., R. D. Vold, and J. W. McBain, *J. Phys. Chem.*, *46*, 429–440 (1942); also Vold, Leggett, and McBain, *ibid.*, *44*, 1058–1071 (1940).
[42] A. Bondi, *J. Chem. Phys.*, *16*, 157–158 (1948).
[43] Compare, for example, K. W. Gardiner, M. J. Buerger, and L. B. Smith, *J. Phys. Chem.*, *49*, 417–428 (1945) and R. H. Ferguson, F. B. Rosevear, and H. Nordsieck, *J. Am. Chem. Soc.*, *69*, 141–146 (1947).

McBain[44] were able to obtain sodium oleate in the form of a viscous liquid, a gel, or a solid, at a single combination of temperature and concentration. Such supercooled gels are not considered essentially different from soap in the liquid form; their sole difference resides in an obscure dissimilarity in structure.
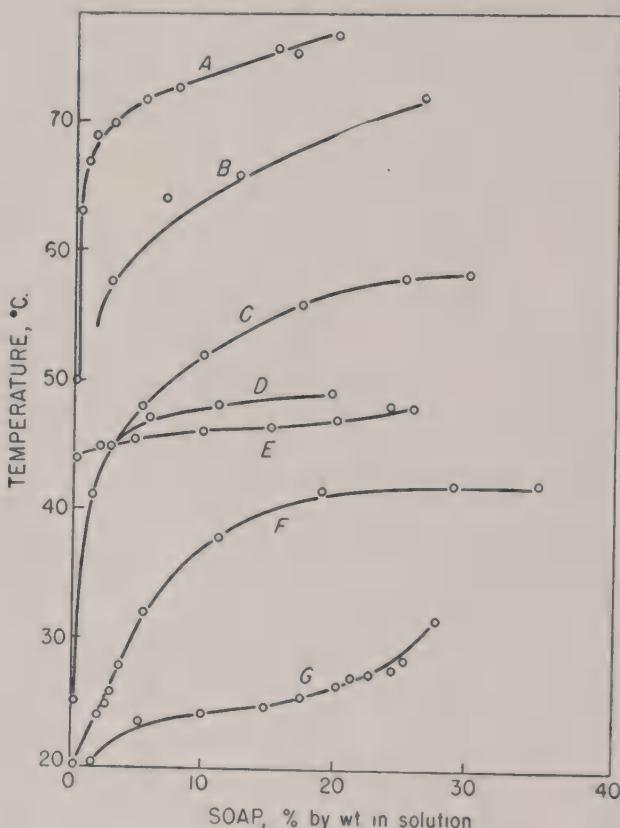
Fig. 51. Solubility of sodium soaps in water: *A*, sodium stearate; *B*, sodium palmitate; *C*, sodium myristate; *D*, commercial tallow soap; *E*, commercial tallow and coconut oil household soap; *F*, sodium laurate; *G*, sodium oleate.[37]

That ordinary solid soaps possess a crystalline structure was first noted by Zsigmondy and Bachmann,[45] from the examination of samples by means of the ultramicroscope. The later ultramicroscopic observations of Darke, McBain, and Salmon[46] emphasized the fibrous nature of the crystals. The same fibrous structure was noticed by Maclennan[24] in his examination of samples at low powers of magnification with polarized

[44] M. E. Laing and J. W. McBain, *J. Chem. Soc.*, *117*, 1508–1528 (1920).
[45] R. Zsigmondy and W. Bachmann, *Z. Chem. Ind. Kolloide*, *11*, 145–157 (1913).
[46] W. F. Darke, J. W. McBain, and C. S. Salmon, *Proc. Roy. Soc. London*, *A98*, 395–409 (1921).

light, and Vold and Ferguson[47] have produced curd fiber bundles of macroscopic size.

2. Phase Behavior of Solid Soaps

It was once believed that all ordinary commercial bar soaps consisted of a felted structure of solid fibers enmeshing a mother liquor of soap solution. However, recent research[48,49] makes it appear that many types of soaps consist solely of solid material. The water associated with soaps of low moisture content must thus be regarded as an integral part of the soap crystal, although its position in the crystal is by no means clear. Thiessen and Erdmann[50] have advanced the highly plausible view supported by x-ray diffraction, electron microscopy, and vapor tension data, that the structure of soap (sodium stearate) crystals is predetermined by the micellar nature of soap in solution (page 361), hence that water in solid soaps is occluded intramicellarly between the hydrophobic CH_3 ends of opposed hydrocarbon chains (see Fig. 55).

Gardiner and co-workers,[51] McBain and Lee,[36] and others have published data which indicate the existence of a large number of soap hydrates. For sodium palmitate, as an example, hydrates containing as little as $1/8$ molecule and as much as 30 molecules of water per molecule of soap have been reported.[52] On the other hand, Ferguson and co-workers,[52] in a careful investigation of sodium palmitate, could find no evidence of the existence of definite hydrates. Their results indicated that water up to 2.5% was in the form of a solid solution in the soap, with increase in water content in this range being accompanied by a smooth increase in the (x-ray) short spacings. Above the 2.5% moisture level, the water was incorporated in such a manner as to not affect the short spacings. Long spacing values were constant at all water levels.

The absorption of water by a soap of low moisture content is accompanied by a considerable evolution of heat, which has caused spontaneous combustion in chips or powders stored in large masses. Heating may occur when lots of different moisture content are mixed and stored.

Soap molecules of different chain lengths mix freely in the crystal lattice, hence commercial soaps crystallize as solid solutions, without fractionation of the individual fatty acids, to form materials which are continuously variable in composition.[48] On the other hand, the so-called acid soaps have been reported to form crystals of chemical individuals

[47] R. D. Vold and R. H. Ferguson, *J. Am. Chem. Soc.*, 60, 2066–2076 (1938).
[48] R. H. Ferguson and H. Nordsieck, *Ind. Eng. Chem.*, 36, 748–752 (1944).
[49] R. H. Ferguson, *Oil & Soap*, 21, 6–9 (1944).
[50] P. A. Thiessen and H. Erdmann, *Z. physik. Chem.*, A193, 367–377 (1944).
[51] K. W. Gardiner, M. J. Buerger, and L. B. Smith, *J. Phys. Chem.*, 49, 417–428 (1945).
[52] R. H. Ferguson, F. B. Rosevear, and H. Nordsieck, *J. Am. Chem. Soc.*, 69, 141–146 (1947).

consisting of compounds of neutral soap and free fatty acid in various fixed ratios.[53]

Thiessen and Spychalski[54] examined stretched filaments of sodium palmitate and determined that the ultimate structural units comprising the fibers consisted of rows of double molecules joined end to end, and oriented perpendicularly to the long axis of the fibers.

Marton and co-workers[55] have applied the electron microscope to the examination of sodium laurate curds. Their remarkably revealing photographs show that the individual fibers are not merely interlaced, but are actually grown together, at angles of less than 90°, and for the most part at angles of 30°, 45°, or 60°. The highly rigid three-dimensional structure of the solid phase accounts for the fact that samples were solid with as little as 12.5% of fibers. The fibers had the form of thin ribbons. The width of the narrowest fibers (42 A.) corresponded closely to the length of two sodium laurate molecules joined end to end, and there was a marked tendency for the widths of the larger fibers to be integral multiples of the same unit.

As mentioned previously, soap fibers readily hydrate, and their properties are affected by the presence of dissolved substances in the liquid with which they are in contact. Salt hardens the fibers, whereas glycerol has a softening effect. The physical characteristics of the finished soap bar are affected by the presence of such substances, as well as the manner in which the soap has been solidified, and by mechanical working of the solidified soap, such as occurs in the milling process.

A matter of very great practical significance is the polymorphism of soap crystals. That certain pure soaps are capable of existence in two distinct crystal forms was discovered by Thiessen and co-workers.[56,57] It is now recognized that there are additional forms, but there is disagreement between the two principal groups of workers in the field as to their number and identity. Originally, Ferguson and co-workers[49,58] reported but four well-defined solid soap phases, which were designated alpha, beta, delta, and omega. On the other hand, Buerger and associates[59-61] have maintained that Ferguson's beta is in reality a mixture of at least two phases, labeled epsilon and zeta, and that his omega comprises two

[53] F. V. Ryer, *Oil & Soap*, *23*, 310–313 (1946).
[54] P. A. Thiessen and R. Spychalski, *Z. physik. Chem.*, *A156*, 435–456 (1931).
[55] L. Marton, J. W. McBain, and R. D. Vold, *J. Am. Chem. Soc.*, *63*, 1990–1993 (1941).
[56] P. A. Thiessen, J. von Kleck, H. Gockowiack, and J. Stauff, *Z. physik. Chem.*, *A174*, 335–358 (1935).
[57] P. A. Thiessen and J. Stauff, *Z. physik. Chem.*, *A176*, 397–429 (1936); *A177*, 398 (1936).
[58] R. H. Ferguson, F. B. Rosevear, and R. C. Stillman, *Ind. Eng. Chem.*, *35*, 1005–1012 (1943).
[59] M. J. Buerger, L. B. Smith, F. V. Ryer, and J. E. Spike, Jr., *Proc. Natl. Acad. Sci. U. S.*, *31*, 226–233 (1945).
[60] M. J. Buerger, *Am. Mineral.*, *30*, 551–571 (1945).
[61] M. J. Buerger, L. B. Smith, and F. V. Ryer, *J. Am. Oil Chem. Soc.*, *24*, 193–196 (1947).

orms to which they have given the names eta and kappa. Additional
orms designated as alpha, beta, gamma, delta, mu, and sigma raise the
otal number recognized by Buerger to ten. More recently, Ferguson
et al.[52] have reported additional detailed data on their beta phase of
odium palmitate, and have reaffirmed their conviction that it is a single
phase and not a mixture, and also that the polymorphism of soaps is to
be interpreted properly in terms of a relatively few basic structures rather
han the great variety of forms proposed by Buerger. Minor differences
n beta phase x-ray diffraction patterns, which led Buerger et al. to
ecognize the two new phases, epsilon and zeta, they attribute specifically
o the above-mentioned effect of water on the short spacings.

The present discussion will be based on the original four forms of
Ferguson and associates, inasmuch as these, whether single phases or
mixtures, have certain distinctive physical characteristics which are im-
portant in practical soapmaking.

The alpha form of sodium soaps, which is in reality a slightly hydrated
phase, reverting to the beta phase on complete dehydration, does not ap-
pear to exist within the range of conditions ordinarily encountered in
commercial soaps. However, the beta, omega, and delta forms are all en-
countered in commercial soaps. They are often somewhat mixed, although
many soaps may be prepared in forms consisting substantially of any one
of the three, according to the conditions accompanying transformation
of the soap to a solid form.

The temperature ranges within which the three forms are stable do not
appear to be clearcut and distinct, but in general they may be said to in-
crease in the order, delta, beta, omega. Spontaneous transformation of
one form to another, in the above order, readily takes place with increase
n temperature. As the soap is cooled, however, transformations in the
opposite direction occur more reluctantly. In some cases spontaneous
transformation does not occur so long as the soap remains in a static con-
dition. Milling, plodding, mixing, extrusion, or other mechanical working
of the material will initiate phase transformation, however, and can gen-
erally be depended upon to produce the soap substantially in the form
which is stable under the conditions of working.

In framed soaps, which are solidified without agitation, the omega
phase is the one chiefly obtained. On the other hand, the beta form is the
predominant form in milled soaps, conversion from the omega form being
produced by milling and plodding. Beta-form soaps may be produced
without milling, however, by quickly chilling neat soap below a critical
temperature at which this form becomes stable, and then agitating the
partially solidified mass to effect the desired conversion from the omega
to the beta form.[62] The critical temperature for any soap varies with
both its fatty acid composition and its moisture content. In the case of

[62] V. Mills (to Procter and Gamble Co.), U. S. Pats. 2.295.594–96 (1942).

20% coconut oil–80% tallow soap of 26% moisture content it is stated to be about 160°F.[62] In soap of lower moisture content, it is higher. Soaps of low molecular weight, such as those made exclusively from coconut oil, either do not transform to the beta phase or transform with extreme slowness. Formation of the omega phase, therefore, is favored by high temperatures, low moisture content, and low molecular weight of the soaps. Transformation of the omega to the beta phase is accomplished by agitating the soap in the range of temperature and moisture content within which the latter phase is stable. In the case of neat soap, conversion to the beta form must proceed in this manner through the omega phase. Systems of higher moisture content may in some cases produce the beta or even the delta phase upon being cooled without agitation.

The delta phase, in contradistinction to the omega phase, tends to be formed under the conditions of low temperature, high water content, and high molecular weight in the soaps. It appears in soaps of high water content upon cooling, and is produced by milling or otherwise working beta-phase soaps at low temperatures, e.g., 50–60°F. Pure coconut oil soaps do not appear to form the delta phase.

Beta-phase soap is chiefly distinguished from omega-phase soap by its property of readily swelling and softening in water. Hence, when it is rubbed with a wet sponge, brush, etc., or agitated in the flake or bead form with water, it lathers more readily than omega soap. It is also slightly firmer than omega soap. Delta soap is intermediate between beta and omega soap in ease of lathering, but is much softer than either of the other two modifications.

The comparative properties of soaps of the three different forms are indicated in Table 86, from the publication of Ferguson, Rosevear, and Stillman.[58] Each of the three soaps mentioned in this table was prepared from the same 20% coconut oil–80% tallow batch. The sample in the beta phase was converted to this form by the operations of milling and plodding. The omega soap was prepared from a bar of the milled soap by heating the latter to 190°F. in a sealed container and allowing

TABLE 86

PROPERTIES OF THREE PHASES OF A TYPICAL COMMERCIAL SOAP[a]

Property	Beta	Omega	Delta
Firmness, arbitrary units.........	8.0	7.2	3.0
Per cent soap rubbed off bar in use in water[b]....................	2.4	0.5	1.7
Reaction to water when soaked...	Swells and disintegrates	No swelling or disintegrating	Cracks with little swelling

[a] R. H. Ferguson, F. B. Rosevear, and R. C. Stillman, *Ind. Eng. Chem.*, *35*, 1005–1012 (1943).

[b] This figure is a measure of the ease of lathering of the bar of soap.

t to cool quietly to room temperature. The delta sample was prepared by reworking the milled soap at 50–60°F.

In addition to its effect on the crystal modification existing in the soap, mechanical working, as in milling, extrusion, etc., hardens the soap and renders it less opaque, through its tendency to produce orientation and compacting of the fibers. In this respect milling is somewhat more effective than is extrusion without milling. Extruded soap bars are said to be 10% more soluble on the side faces than on the end faces, through orientation of soap fibers.[62]

3. NATURE OF DILUTE SOLUTIONS

Of somewhat greater importance than the physical behavior of concentrated forms is the behavior of soaps and other surface-active agents in the form of the dilute solutions commonly used for detergent operations in the household and in industry.
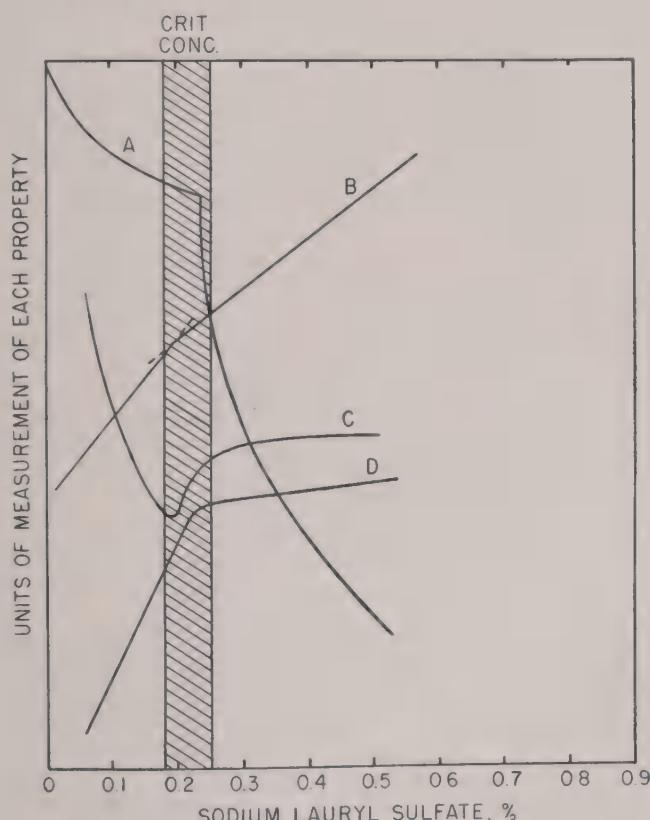
Fig. 52. Discontinuities in the: (A) equivalent conductivity, (B) density, (C) surface tension, and (D) osmotic pressure, of sodium lauryl sulfate at the critical concentration for micelle formation (adapted from Preston[4a]).

The early work of McBain and others rendered it apparent that there is some species of ionic aggregation in soap solutions. The electrical conductivity of moderately concentrated soap solutions is much greater than is to be expected from their content of crystalloid material, as indicated by osmotic or freezing point methods. This would suggest the presence of particles carrying a multiplicity of electrical charges. The transport number data furnish further evidence of ionic association. As the concentration of the solutions is increased, migration of the fatty acid radical increases abnormally, indicating the formation of ionic aggregates of high mobility.

There are other peculiarities in the manner in which the equivalent conductivity of soap and other detergent solutions changes with concentration of the solution. Very dilute solutions behave not very differently from ordinary electrolytes, with the conductivity and the freezing point lowering decreasing normally with increase in concentration. At a certain critical concentration, however, the conductivity begins to decrease very rapidly with increasing concentration of the solution, and thereafter it passes through a minimum, and then slowly increases. Near the same critical point, minima appear in the surface and interfacial tensions of the solution (Fig. 52), the osmotic pressure begins to rise less rapidly with increase in concentration, and discontinuities appear in the curves representing concentration *vs.* such properties as density,[63,64] viscosity,[64,65] and refractive index.[66,67]

It is now universally accepted that the narrow concentration range in which the different points of inflection occur is coincident with the beginning of the large-scale formation of colloidal or micellar particles; hence reference is commonly made to the *critical concentration for micelle formation.* This concentration is usually determined by conductivity measurements, although it is also indicated by the break in the curve for any of the properties mentioned above. In addition, as will be discussed in more detail later, the micelles have the power of holding oil-soluble material, virtually in hydrocarbon solution, between the hydrocarbon chains directed toward the interior of the particle. A recent simple but fairly accurate and widely used technique for the determination of critical concentrations makes use of the discovery that certain organic dyes have different absorption spectra in polar (water) and nonpolar (hydrocarbon) solvents, apparently through association of the molecules to a dimeric form in the former. As the concentration of dissolved material in a dilute aqueous solution of the dye is increased, the beginning of ex-

[63] K. Hess, W. Philippoff, and H. Kiessig, *Kolloid-Z.*, *88*, 40–51 (1939).
[64] K. A. Wright and H. V. Tartar, *J. Am. Chem. Soc.*, *61*, 544–549 (1939).
[65] W. Philippoff, *Kolloid-Z.*, *96*, 255–261 (1941).
[66] H. B. Klevens, *J. Chem. Phys.*, *14*, 567–568 (1946).
[67] H. B. Klevens, *J. Phys. Colloid Chem.*, *52*, 130–148 (1948).

tensive micelle formation is announced by a characteristic color change.[68]

Reference has been made earlier (page 349) to the peculiar form of the solubility curves of soaps. The curves for other micelle-forming colloids are similar. Over a certain range of temperature and concentrations the solubility increases normally with increase in the temperature. Then at a certain point, there is an enormous increase in solubility in a
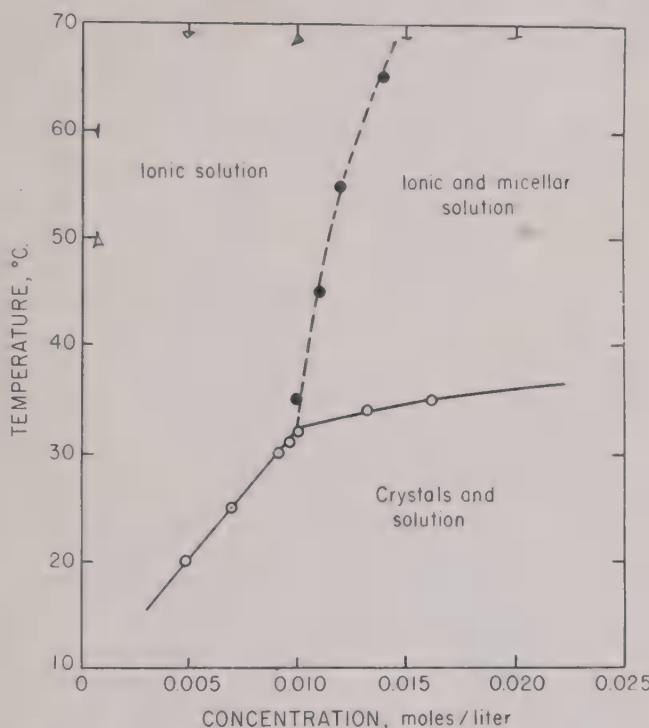
Fig. 53. Phase diagram for low concentrations of sodium lauryl sulfonate and water, showing relationship between solubility and critical concentration for micelle formation. Open circles represent solubilities, according to Tartar and Wright[69]; closed circles represent critical concentrations for micelle formation, according to Klevens.[67]

very short temperature interval. When the critical concentration for micelle formation is plotted as a function of temperature, a curve is obtained which may be regarded as an upward extension of the steep (and normal) portion of the solubility curve (Fig. 53).[67,69] This suggests very strongly that in the last analysis micelle formation and the deposition of visible crystals are different manifestations of the same phenom-

[68] M. L. Corrin, H. B. Klevens, and W. D. Harkins, *J. Chem. Phys.*, *14*, 216–217, 480–486 (1946). M. L. Corrin and W. D. Harkins, *J. Am. Chem. Soc.*, *69*, 679–683 (1947). See also S. E. Sheppard and A. L. Geddes, *J. Chem. Phys.*, *13*, 63–65 (1945). For details of the original solubilization method, based upon the *amount* of dye solubilized at different concentrations, see G. S. Hartley, *J. Chem. Soc.*, *1938*, 1968.
[69] H. V. Tartar and K. A. Wright, *J. Am. Chem. Soc.*, *61*, 539–544 (1939)

enon, and that large-scale micelle formation simply begins when the true solubility of the nonassociated material is exceeded. Further support for this viewpoint is seen in the considerable amount of evidence[70] that there is no further increase in the concentration of nonassociated long chain ions (or molecules) after the critical concentration is reached.

From a practical standpoint, the important conclusion to be derived from the above is that the effective concentration of a surface-active agent is always limited by solubility considerations, whether arrival at the limits of solubility is manifested visibly—by the appearance of macroscopic crystals—or invisibly—by the formation of submicroscopic micelles. As pointed out previously (page 330), it is only the unmicellated material that has surface activity.[73a]

As would be expected, the critical concentration for micelle formation decreases regularly with increase in chain length in any homologous series of surface-active compounds; typical data on different compounds, taken from the work of Klevens,[67] Haffner et al.,[71] Scott and Tartar,[72] and Ralston and co-workers[73] are shown graphically in Figure 54. The critical concentration is only slightly temperature-dependent (Fig. 53), and it may be decreased as much as several-fold by the addition to the solution of neutral noncolloidal electrolytes. The critical concentration of potassium laurate, for example, was found to be decreased from 0.022 to 0.012 mol per liter by the addition of 0.1 mol per liter of potassium nitrate, and to 0.0055 mol per liter by the addition of 0.5 mol per liter of the latter.[74] It has been shown that the effect of different added salts upon the critical concentration,[75] as well as upon the surface tension of the solution,[75] is unrelated to the nature of the ion bearing a charge similar to the long chain ion, and is dependent only upon the concentration of ions of opposite charge. A recent treatment of the theory of this "salt effect" has been presented by Corrin and Harkins.[75]

In a mixture of surface-active agents the critical concentration for micelle formation is intermediate between the concentrations for the individual components.[67]

Soaps are inclined to hydrolyze in acid solution, to form free fatty acids or acid soaps. Even in pure water sufficient hydrolysis may occur to affect the surface activity of relatively dilute solutions, with hydrolysis

[70] See, for example, R. C. Murray, Trans. Faraday Soc., 31, 206 (1935); W. C. Preston, J. Phys. Colloid Chem., 52, 84–97 (1948); I. M. Kolthoff and W. F. Johnson. ibid., 52, 22–27 (1948).

[71] F. D. Haffner, G. A. Piccione, and C. Rosenblum, J. Phys. Chem., 46, 662–670 (1942).

[72] A. B. Scott and H. V. Tartar, J. Am. Chem. Soc., 65, 692–701 (1943).

[73] A. W. Ralston, C. W. Hoerr, and E. J. Hoffman, J. Am. Chem. Soc., 64, 97–101 (1942). A. W. Ralston and C. W. Hoerr, ibid., 64, 772–776 (1942).

[73a] In this connection, see R. C. Murray, Trans. Faraday Soc., 31, 206–212 (1935); I. Traube, ibid., 31, 1730–1739 (1935); and also Hartley (footnote 4), and Preston (footnote 4a).

[74] I. M. Kolthoff and W. F. Johnson, J. Phys. Colloid Chem., 52, 22–27 (1948).

[75] M. L. Corrin and W. D. Harkins, J. Am. Chem. Soc., 69, 683–688 (1947).

tending to become more marked as the chain length of the soap increases. Hydrolysis is repressed by the presence of alkaline compounds.

It was once believed that the free alkali formed as the result of hydrolysis in soap solutions played a major role in detergent action. However, the work of McBain and Martin[76] showed that extensive hydrolysis did not occur, and that the detergent action of soap must be largely physical in nature. McBain and Martin concluded that hydrolysis produced only acid soaps of very low solubility and poor detergent properties.
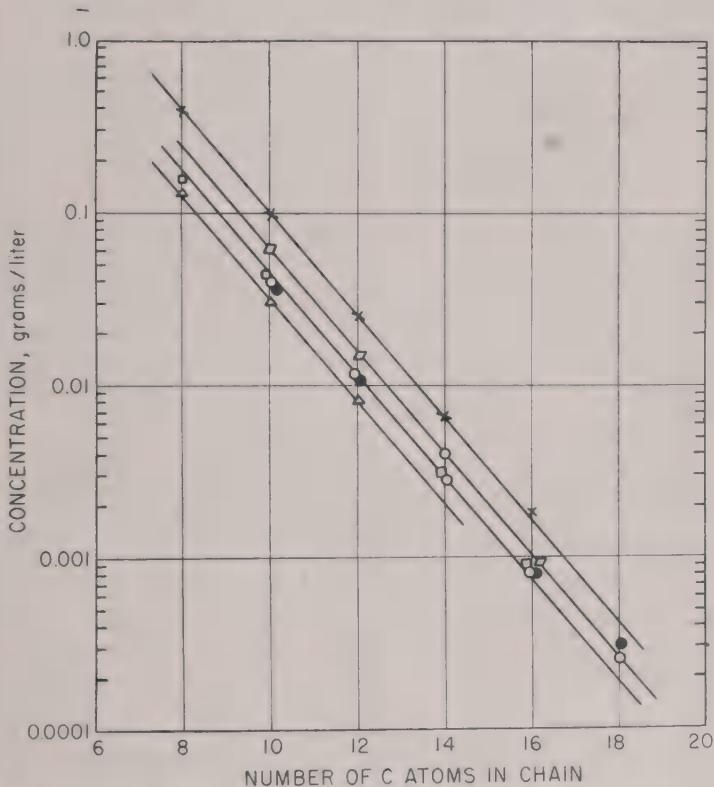
Fig. 54. Relation of critical concentration for micelle formation to chain length for different surface-active materials: x, potassium soaps (refractive index[67]); □, sodium alkyl sulfonates (refractive index)[67]; △, sodium alkyl sulfates (conductivity)[71]; ◇, alkyl trimethylammonium bromides (conductivity)[72]; ○, alkyl amine hydrochlorides (refractive index)[67]; ●, alkyl amine hydrochlorides (conductivity).[73]

Late investigations[77] have produced data to modify considerably McBain's original conclusions. Whereas it was formerly assumed that only simple ions were hydrolyzed, and that acid soaps were produced by secondary reaction, it is now postulated by Ekwall[78] that there is stepwise association in the solution according to the concentration of the latter

[76] J. W. McBain and H. E. Martin. *J. Chem. Soc.*, *105*, 957–977 (1914).
[77] P. Ekwall, *Kolloid-Z.*, *77*, 320–323 (1936); *80*, 77–100 (1937); *85*, 16–24 (1938); *92*, 141–157 (1940). J. Powney and D. O. Jordan, *Trans. Faraday Soc.*, *34*, 363–367 (1938). J. Stauff, *Z. physik. Chem.*, *A183*, 55–85 (1938); *A185*, 45–59 (1939).
[78] P. Ekwall, *Kolloid-Z.*, *92*, 141–157 (1940).

and that the association products hydrolyze directly, to yield a variety of hydrolysis products. Hydrolysis occurs more readily as association increases. The course of hydrolysis of a sodium laurate solution at 20°C. is represented by Ekwall and Lindblad[79] to be as follows: At the highest dilutions, the degree of hydrolysis decreases normally as the concentration increases. Below a limiting concentration of about 0.006 N, hydrolysis produces two univalent ions, and forms free lauric acid. When the solution becomes saturated with lauric acid, and this acid begins to separate, the degree of hydrolysis becomes constant. Immediately above the limiting concentration, hydrolysis produces double ions of the relatively insoluble acid soap, NaLHL. At a concentration of about 0.0075 N, crystals of the insoluble acid soap begin to separate, and at the same time the degree of hydrolysis begins to rise. Hydrolysis at this point appears to produce triple ions of a soluble crystalline liquid acid soap. At a concentration between 0.021 and 0.022 N, quadruple laurate ions begin to be produced, from acid soaps of the formula 3 NaLHL, and the degree of hydrolysis again increases. Beyond a normality of 0.03, there is further association and increase in the degree of hydrolysis, and it is only at a normality of about 0.06 that the degree of hydrolysis finally begins to fall off.

According to Powney and Jordan,[79a] in a sodium palmitate solution at 60°C. hydrolysis is at a minimum (*ca.* 4%) at a concentration between 0.0001 and 0.001 molar, and at a maximum (*ca.* 17%) between 0.001 and 0.01 molar.

The data of Powney and Jordan were analyzed by Stainsby and Alexander,[79b] who attribute the increase in hydrolysis with increase in concentration to solubilization of undissociated fatty acid in soap micelles, with consequent displacement of the equilibrium between free and combined acid.

Recently, however, the hydrolysis of soaps has again been examined by McBain and co-workers,[80] who reaffirm their opinion that free fatty acids never separate from solution in the absence of another acid. Few of the common surface-active agents other than soap hydrolyze to any appreciable degree.

4. STRUCTURE OF MICELLES AND SOLUBILIZATION

Controversy still exists concerning the nature and structure of the aggregates of material in a colloidal electrolyte solution. In the case of the more dilute solutions, all evidence of structure is purely indirect; at

[79] P. Ekwall and L. G. Lindblad, *Kolloid-Z.*, *94*, 42–57 (1941).
[79a] J. Powney and D. O. Jordan, *Trans Faraday Soc.*, *34*, 363–371 (1938).
[79b] G. Stainsby and A. E. Alexander, *Trans. Faraday Soc.*, *45*, 585–597 (1949).
[80] J. W. McBain, P. Laurent, and L. M. John, *J. Am. Chem. Soc.*, *25*, 77–84 (1948).

relatively high concentrations some direct indications are provided by x-ray data.

Any theory of micelle structure must explain, not only the abrupt change in conductivity, etc., at the so-called "critical concentration," but also the fact that at higher concentrations there is a leveling off of the first abrupt effect and, in many cases, eventually even a reversal in trend of the curve in question. Most of the present controversy revolves around opposed views of Hartley and McBain. Hartley[4] and others[72] consider it neccessary to postulate but a single type of micelle consisting of long
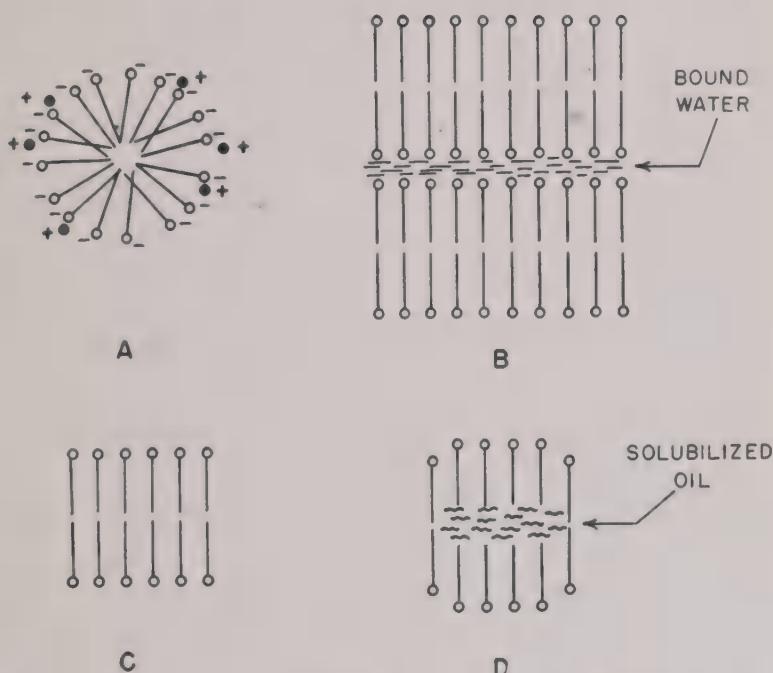
Fig. 55. Possible micelle forms: (A) spherical micelle with attached gegenions of Hartley, (B) "neutral" lamellar micelle of McBain, (C) cylindrical micelle of Harkins, (D) cylindrical micelle with solubilized oil.

chain ions oriented toward a common center to form a spherical particle (Part A, Fig. 55). The various conductivity effects, etc., can be explained on the assumption that small oppositely charged ions or "gegenions" attach themselves to the surface of the particle and that the number attached varies as the temperature and concentration of the solution is changed. McBain,[81] on the other hand, conceives of an additional micelle form, of lamellar structure, made up of layers of neutral oriented molecules (Part B, Fig. 55). The various electrical effects are explained

[81] See any one of numerous late publications of J. W. McBain, and associates, e.g., Chapter 3 in *Colloid Chemistry*, Vol. V, J. Alexander, ed., Reinhold, New York, 1944.

upon the basis of shifting equilibrium among the three forms consisting of simple long chain ions, ionic micelles, and lamellar micelles. Recently, Harkins and co-workers[82] have set up a slightly modified lamellar or "cylindrical" model for the small micelle, but have denied the concept of "bound water" layers between the hydrophilic groups of the opposed hydrocarbon chains, attributing to each micelle instead only a single double layer of ions or molecules (Part C, Fig. 55).

According to calculations made by Debye,[82a] based on light scattering in solutions, the micelles (of cationic compounds of 10–14 carbon atoms) are made up of aggregations of an average of 40–140 ions, with the number increasing with increasing chain length, or with the addition of a neutral electrolyte.

At quite high concentrations of the surface-active agent (e.g., 3–7% by weight, as compared to 0.005–0.5% by weight at the critical concentration for micelle formation), aqueous solutions begin to exhibit characteristic x-ray diffraction bands which have appeared to constitute good evidence of a layer structure. When an oily compound is then solubilized by the solution there is an increase in the x-ray spacings, which is a logical expectation if the oil is to be enclosed in the form of a layer between the lipophilic ends of the long chains in a lamellar micelle (Part D, Fig. 55).

Although the lamellar structure for micelles in concentrated solutions has been generally accepted, upon consideration of the x-ray evidence, it has recently been shown by Corrin[83] that the latter is by no means decisive, inasmuch as all of the x-ray data can be explained upon the basis of a spherical micelle model.

It has long been known that soap solutions are capable of dissolving appreciable amounts of organic liquids which are almost insoluble in water alone.[84]

Regardless of the true form of the soap micelle, it is generally agreed that solubilization of an oil, to form an optically clear solution, must proceed by enclosure within the lipophilic interior of the micelles. In many cases considerable quantities of oil are dissolved. Solubilization begins at low concentrations of the surface agent, before the above-mentioned x-ray spacings appear, or even before the critical concentration for micelle formation is reached. As would be expected, it is influenced by the presence of neutral electrolytes, and the solubilizing

[82] W. D. Harkins, *J. Chem. Phys.*, *16*, 156–157 (1948). R. W. Mattoon, R. S. Stearns, and W. D. Harkins, *ibid.*, *16*, 644–658 (1948).

[82a] P. Debye, *J. Phys. Colloid Chem.*, *53*, 1–8 (1949).

[83] M. L. Corrin, *J. Chem. Phys.*, *16*, 844–845 (1948). See also G. S. Hartley, *Nature*, *163*, 767–768 (1949).

[84] See, for example, S. U. Pickering, *J. Chem. Soc.*, *111*, 86–101 (1917); C. R. Bailey, *ibid.*, *123*, 2579–2590 (1923); E. L. Smith, *J. Phys. Chem.*, *36*, 1401–1418, 1672–1684, 2455–2473 (1932).

capacities of different agents for specific oils present a complex picture. For detailed information on quantitative relationships and other aspects of the phenomenon, reference should be made to such publications as those of Smith,[85] McBain and Johnson,[86] and McBain and Richards.[87]

A phenomenon which is superficially similar to solubilization but actually somewhat different is the blending of two normally immiscible organic liquids, such as glycols and hydrocarbons, with the assistance of soaps or other surface-active agents. In this process there is not necessarily any formation of micelles, and the soap molecules merely serve to offer a bridge between dissimilar molecules of the two liquids.[88]

5. Surface and Interfacial Tensions

The effect of a typical surface-active agent (sodium lauryl sulfate) on the surface tension of pure water and on the interfacial tension of water against xylene is shown in Figure 56.[89] When this compound is highly purified the minimum in the surface tension curve becomes much less pronounced,[90] and it is claimed that it is thus a characteristic of mixed materials.[90a] Most, though not all surface-active materials exhibit minima as shown in the figure, which coincide with the beginning of the large-scale development of micelles (compare Fig. 52, page 355). Ordinary soaps lower the interfacial tension of water against fatty oils to 2–5 dynes when present to the amount of 0.1%.

Mention has been made previously (page 358) of the effect of added salts or other electrolytes in lowering the critical concentration for micelle formation. That the addition of electrolytes to a surface-active solution will lower the surface tension has often been observed, and it appears that a similar effect occurs in the case of interfacial tensions. Robinson,[14] for example, found that electrolytes had a marked effect upon the interfacial tension of sodium alkyl sulfate and Igepon solutions against transformer oil. The effect was independent of the nature of the anion; equimolar solutions of NaCl, NaOH, etc., lowered the interfacial tension to an equal degree. The valency of the cation had a large influence, however. $LaCl_3$ was more effective than $CaCl_2$, which was in turn more effective than NaCl in decreasing the interfacial tension. The influence of the dissolved electrolytes was attributed to their probable effect of reducing the mutual repulsion of adsorbed detergent molecules at the in-

[85] E. L. Smith. *J. Phys. Chem.*, *36*, 1401–1418 (1932).
[86] J. W. McBain and K. E. Johnson, *J. Am. Chem. Soc.*, *66*, 9–13 (1944).
[87] J. W. McBain and P. H. Richards, *Ind. Eng. Chem.*, *38*, 642–650 (1946).
[88] S. R. Palit and J. W. McBain. *Ind. Eng. Chem.*, *38*, 741–744 (1946).
[89] J. Powney and C. C. Addison, *Trans. Faraday Soc.*, *33*, 1243–1253 (1937).
[90] G. D. Miles and L. Shedlovsky, *J. Phys. Chem.*, *48*, 57–62 (1944). L. Shedlovsky, J. Ross, and C. W. Jakob. *J. Colloid Sci.*, *4*, 25–33 (1949).
[90a] In this connection, see also D. Reichenberg, *Trans. Faraday Soc.*, *44*, 467–478 (1947).

terface. This would permit closer packing of the latter, with a consequent further lowering of the interfacial tension. It is quite in accord with this explanation that in solutions of cationic compounds (with the long chain portion positively charged) it is the anion of the added electrolyte that determines the extent to which surface activity is increased, and that solutions of nonionic agents are relatively unaffected by electrolytes.

Relatively little has been published concerning the surface activity of the usual surface-active agents in nonaqueous solvents. In some cases,
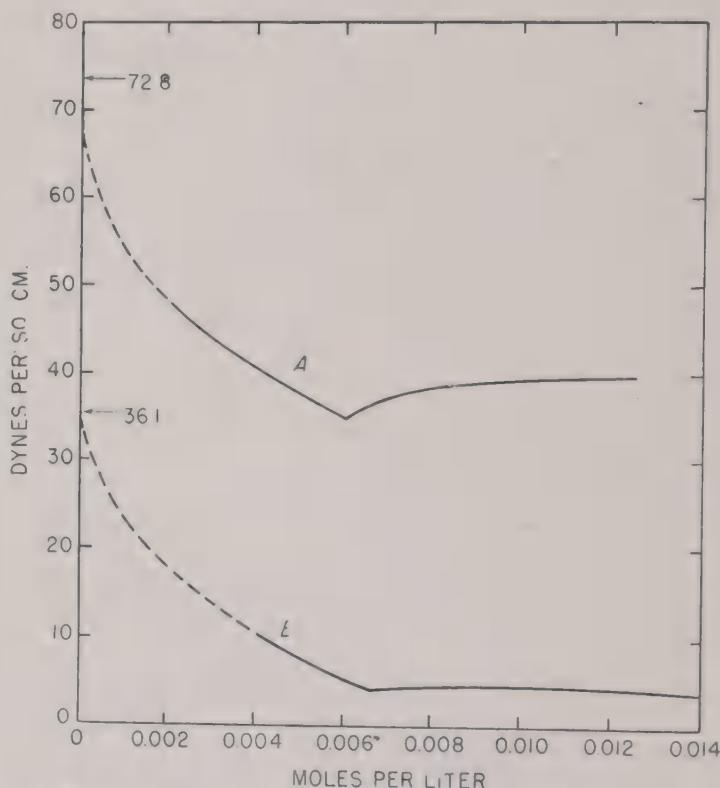
Fig. 56. Effect of sodium dodecyl sulfate on (A) the surface tension of pure water and (B) the interfacial tension of water against xylene.[89]

at least, a more or less normal lowering of the surface tension occurs.[91] However, it is to be noted that the various oil-soluble monoglycerides, which are very effective in lowering the interfacial tension between a fatty oil and water, have little effect upon the surface tension of the fat. Because at an oil–water interface both hydrophilic and lipophilic tendencies come into play, and because of the importance of the balance between these two characteristics, it is probably not to be expected that there will generally be a parallelism between surface tension and inter-

[91] J. W. McBain and L. H. Perry, J. Am. Chem. Soc., 62, 989–991 (1940).

facial tension effects. Ralston and co-workers[92] have shown that in aqueous ethanol the solubility curves of dodecylamine hydrochloride indicate a disappearance of micelle formation when the alcohol concentration becomes high.

It has been known since the time of Rayleigh that there may be a great difference between the "dynamic" surface or interfacial tension of a surface just formed and the "static" tension of an old surface in equilibrium with the surface-active agent. The difference is, of course, an essential condition of the tendency of such agents to concentrate at surfaces. Migration to the surface from the bulk of the liquid and orientation at the surface of course require time. For data on the rate at which equilibrium is attained in typical systems, reference may be made to such publications as those of Nutting and co-workers,[93] Dreger and co-workers,[94] Adam and Shute,[95] and Alexander.[96]

D. Commercial Soap Products

1. RAW MATERIALS

(a) Fats and Other Saponifiable Materials

The oils and fats which serve as raw materials for the manufacture of soaps are to be considered principally from the standpoint of their fatty acid composition. Glyceride structure is of no consequence in soapmakers' fats. The natural antioxidants which are such important constituents of edible oils and fats are probably to some extent lost in the saponification process, and in any event a wide variety of artificial antioxidant materials are available for addition to soaps, since antioxidants for soaps are not required to be edible. The coloring materials present in fats are of some consequence, inasmuch as they are partially carried into the finished soap.

Aside from fats, the only saponifiable material used to any extent in soap is rosin. This material was heavily depended upon at one time by United States soapmakers, but its use has declined, and in late years the total amount consumed has not amounted to more than about 5% of the consumption of fats.

In the case of soaps made experimentally from single fatty acids, both the surface-active properties of the soap and its solubility will be found

[92] A. W. Ralston and C. W. Hoerr, *J. Am. Chem. Soc.*, *68*, 851–854 (1946).
[93] G. C. Nutting, F. A. Long, and W. D. Harkins, *J. Am. Chem. Soc.*, *62*, 1496–1504 (1940). G. C. Nutting and F. A. Long, *ibid.*, *63*, 84–88 (1941).
[94] E. E. Dreger, G. I. Keim, G. D. Miles, L. Shedlovsky, and J. Ross, *Ind. Eng. Chem.*, *36*, 610–617 (1944).
[95] N. K. Adam and H. L. Shute, *Trans. Faraday Soc.*, *34*, 758–765 (1938).
[96] A. E. Alexander, *Trans. Faraday Soc.*, *37*, 15–25 (1941).

to be highly dependent upon the length of the fatty acid chain and its degree of unsaturation. It is not surprising therefore, that the fatty acids which may be regarded as really desirable materials for sodium soap manufacture are quite restricted in number. Specifically, they consist of the saturated acids with 12 to 18 carbon atoms, i.e., lauric, myristic, palmitic, and stearic acids, and oleic acid. Acids with less than 12 carbon atoms are insufficiently high in molecular weight to possess good surface activity, and acids containing more than 18 carbon atoms are too nearly insoluble in water at ordinary temperatures to be useful. Sodium oleate has good detergent properties, comparable to those of sodium stearate. It has the advantage over sodium stearate of being much more soluble at ordinary temperatures and the disadvantage of being unsaturated and hence somewhat susceptible to oxidation. However, linoleic, linolenic, and other more unsaturated fatty acids, produce soft soaps which not only are easily oxidized, but are also relatively poor detergents, presumably because a multiplicity of double bonds in the fatty acid chain interferes with proper surface orientation of the soap molecules. Neither ricinoleic acid nor the iso-oleic acids produced by hydrogenation are considered desirable in soaps.

Unsaturated acids produce soaps which are inclined to be somewhat sticky, and which give an undesirably "greasy" lather.

Soaps made from the higher fatty acids (e.g., stearic) are very efficient detergents. However, the fact that they are soluble but to a limited extent in cold or warm water limits their usefulness as ordinary household soaps. Soaps of the lower fatty acids (e.g., lauric acid) are freely soluble and yield a profuse, if somewhat unstable lather. However, they are less efficient in their detergent action than soaps of higher fatty acids. Although they lather readily from a bar or other solid form, their sudsing properties in solution are relatively poor. In practice, a soap actually has two functions, i.e., a certain portion of it must serve as a water softener before the remainder can function as a detergent. Considerably larger quantities of lower molecular weight soaps are required for a given degree of water softening, as compared with soaps of high molecular weight.

The optimum balance between high solubility and free lathering on one hand, and lasting lather and good sudsing, with high detergent activity and good water softening capacity on the other, is probably attained in soaps of myristic (C_{14}) acid. Unfortunately, no fat containing a high percentage of this acid is available in large quantities. In practice, therefore, the above-mentioned balance is obtained by using fats which yield a proper mixture of lauric, palmitic, stearic, and oleic acids, with other acids of course being present in minor proportions. Thus the standard fat mixture for the production of the higher grade household soaps has for many years consisted of tallow, palm oil, hydrogenated marine oils,

and other fats of high molecular weight mixed with 15 to 30% of coconut or palm kernel oil.

Under ordinary conditions, both coconut and other free-lathering oils, and tallow and other slow-lathering oils are available in quantities sufficient to maintain the proper balance between the two classes of ingredients. In the absence of a free supply of coconut-type oils, soapmakers may incorporate considerable amounts of potassium soaps into their products. The use of a moderate amount of potassium soap in a product made from tallow or similar fats has the effect of solubilizing it and to some extent conferring upon it the properties of a tallow-coconut oil soap, without making it markedly softer.

The fats and oils used in soap manufacture are in general low-grade products, which sell at prices substantially below those commanded by edible animal fats, drying oils, or the more choice nondrying vegetable oils. Up to the present time there has been only a very minor consumption in soap manufacture of lard, edible olive oil, cottonseed oil, peanut oil, soybean oil, linseed oil, or any other oil or fat held in the highest esteem for edible use or for paint manufacture.

The amounts of the various fats and oils consumed in the manufacture of soap in the United States in 1947 are listed in Table 87. It will be noted that of 2,354,594 thousand pounds of fats consumed, 1,526,169 thousand pounds, or 65% consisted of inedible animal fats, i.e., tallow and grease. More than half the remainder, or about 22% of the total, consisted of coconut oil. European soapmakers are accustomed to using lesser proportions of animal fats and correspondingly greater proportions of vegetable oils. In Great Britain the vegetable oils consist chiefly of palm oil, palm kernel oil, hydrogenated whale oil, and other fats which produce hard soaps, but in other European countries there is a considerable consumption of soft vegetable oils.

Tallow has long been the basic ingredient of the soap made in the United States. Tallow soap is firm, has good keeping qualities, and is an efficient cleaning material. Tallow is used as the sole fat in the manufacture of bulk chips for use by commercial laundries, but in most other soap products it is mixed with coconut oil, in order to improve the solubility and lathering properties of the soap. It must be refined and more or less drastically bleached before it is charged to the soap kettle, but is not ordinarily subjected to other treatment.

Greases are less desirable soap fats than tallow. They are higher in iodine value and consequently produce a softer soap with poorer keeping qualities. They are often subjected to slight hydrogenation, to make them more closely resemble tallow, before use. The darker grades, like tallow, are bleached, and very low-grade greases, such as garbage or

extraction greases are often split and their fatty acids distilled for use in soap.

Whale and fish oils are invariably hydrogenated, to the approximate consistency of hard tallow, before they are used in soaps. However, fish oil which has been sufficiently hardened to eliminate permanently its objectionable odor produces a soap which is even less soluble than tallow soap. It is consequently blended with softer oils or coconut oil, or both, for soapmaking purposes.

TABLE 87

FATS AND OTHER SAPONIFIABLE MATERIALS USED IN MANUFACTURE OF SOAPS IN UNITED STATES IN 1947[a]

Item	Quantity, 1000 lbs.
Tallow, inedible	1,108,909
Whale and fish oils	42,550
Grease	417,260
Palm oil	1,091
Tallow, edible	7,087
Lard and rendered pork fat	5,973
Coconut oil	511,313
Babassu oil	14,581
Secondary fats and oils[b]	227,847
Olive oil, foots and inedible	764
Soybean oil	5,375
Cottonseed oil	920
Corn oil	446
Castor oil	9,041
Linseed oil	276
Peanut oil	374
Sesame oil	8
Oleo oil	40
Olive oil, edible	4
Neatsfoot oil	23
Other vegetable oils	712
Total fats and oils	*2,354,594*
Rosin	79,866
Tall oil	16,329
Total saponifiable materials	*2,450,789*

[a] U. S. Dept. Agr., *Agricultural Statistics*, 1948.
[b] Includes fatty acids, soapstock from alkali refining, stearine from pressing of animal fats, etc.

Soap prepared exclusively from palm oil is said to be inclined to be somewhat hard and crumbly, hence is customarily mixed with coconut oil soap, either alone or in combination with soap from tallow or softer fats or oils. Although the very dark orange-red color of palm oil may be bleached by suitable methods, it is difficult to prepare a very white soap containing a large percentage of this oil.

Because of its high content of lauric acid, coconut oil is ordinarily considered an essential ingredient of toilet soaps, packaged flakes, beads, etc., and other products in which ready solubility and good lathering are important. Palm kernel oil and babassu oil, cohune oil and other kernel oils of American palms are similar in fatty acid composition to coconut oil, and confer the same properties upon the soaps in which they are used. Palm kernel oil has never been widely used in the United States, but in Europe its use is rather more common than that of coconut oil. The American palm kernel oils have recently become a considerable factor in soap production in the United States.

Oils of the coconut type are not ordinarily used alone except in the manufacture of special soaps for use with very hard water or sea water, in which lathering ability and electrolyte stability are all-important. Coconut oil soap is ordinarily very white, is extremely resistant to oxidation, and is firm in consistency. The presence of this oil in high-grade milled toilet soaps is considered to contribute to the polished appearance which is desired in the finished bars.

To the skin of some people coconut oil soaps are somewhat irritating. In a study of the soaps of various pure fatty acids Emery and Edwards[97] found, somewhat surprisingly, that the chief offenders in this respect are not the low molecular weight fatty acids, caprylic and capric, but lauric, the medium molecular weight acid, and to a lesser degree, myristic acid. McKinney and Edwards[98] found the soaps of mixed lauric and caprylic acids to be highly irritant, whereas in general the admixture of higher acids, including myristic, oleic, and linoleic, made lauric acid soaps less irritating. As a soapmaking material, coconut oil fatty acids are said to be improved in mildness as well as other respects by fractionation to remove the fatty acids below C_{12}.[99]

In the United States the various liquid oils, such as olive oil, cottonseed oil, peanut oil, corn oil, soybean oil, etc., may be classed as very minor contributors to the soap kettle. The greatest portion of these oils is consumed in the form of foots or acidulated foots from the alkali refining of cottonseed and soybean oils. The foots are a by-product of the refining of these oils for edible purposes and are consumed in soap merely because they are unsuitable for most other purposes. They go largely into the manufacture of low-grade washing powders, cleansers, etc.

In some products, notably the liquid potash soaps used for washing automobiles and painted and linoleum surfaces, a drying or semidrying oil such as linseed, soybean, or corn oil is a desirable ingredient.

Rosin, which is composed principally of abietic acid, is generally con-

[97] B. E. Emery and L. D. Edwards. *Oil & Soap*, *17*, 64–66 (1940).
[98] M. W. McKinney and L. D. Edwards. *Oil & Soap*, *23*, 198–200 (1946).
[99] B. J. Grondal and H. M. Wylde (to Lever Bros. Co.), U. S. Pat. 2,300,416 (1942).

sidered an inferior soapmaking material, even though rosin soaps have certain desirable properties, such as high solubility, superior germicidal action,[100] a high capacity for silicate fillers,[39] and an antioxidant action in small concentrations.[101]   Their chief disadvantage is their low resistance toward oxidation, which is associated with a natural yellowish color and color instability. They are also deficient in water softening power,[102] and are inclined to be soft and sticky. The principal use of rosin is in yellow laundry soaps.

Rosins modified by hydrogenation, dehydrogenation, or polymerization are now available which are said to combine the advantageous features of ordinary rosin with greatly increased stability toward oxidation and discoloration.[103]

(b) Other Raw Materials

Besides the saponifiable materials mentioned above, the most important raw material used by soapmakers is caustic soda. Soda ash will not saponify glycerides, but is used to some extent in saponifying fatty acids, and is also used in large quantities as a builder in laundry soaps. Caustic potash is employed almost exclusively in making soft soaps, although potassium carbonate, like sodium carbonate, may be used to saponify fatty acids. It is important for the alkalies used for saponification to be as free as possible from iron or other heavy metals, as these may cause the soap to discolor, and some have a deleterious effect upon the resistance of the soap to oxidation.

An important class of laundry soap constituents is comprised of the so-called soap builders. These consist of certain sodium salts of weak inorganic acids, which are alkaline in solution. The most commonly employed builders are soda ash, the various sodium silicates, trisodium phosphate, tetrasodium pyrophosphate, sodium hexametaphosphate, and, more recently, sodium tripolyphosphate. The builders are in general less expensive than soap, and hence may be used merely to cheapen the product. It is well established, however, that certain builders contribute significantly to the detergent action of soap, and they have important auxiliary functions.

Mention has been made previously of the effect of electrolytes in enhancing the surface activity of soaps and similar compounds, and of the desirability of buffering soap solutions at a high pH (10–11) to repress hydrolysis. The literature on sodium silicates in soaps, which is more extensive than that relating to other builders, has recently been

[100] L. S. Stuart and W. D. Pohle, Oil & Soap, 18, 2–7 (1941).
[101] A. Campbell, Ind. Eng. Chem., 26, 718–719 (1934).
[102] E. E. Ruff, Oil & Soap, 22, 125–127 (1945).
[103] B. S. Van Zile and J. N. Borglin, Oil & Soap, 22, 331–334 (1945).

reviewed by Merrill.[104] The silicates are in themselves efficient suspending and deflocculating agents,[105-107] and are recognized as having a marked antioxidant action on soaps to which they are added. The sodium silicate usually used by soapmakers is in the form of a solution with a specific gravity of 41° Bé. and has a silica to alkali ratio (SiO_2 to Na_2O) of 3.2 to 1.

An extremely important function of soap builders is their softening of hard waters. Silicates and phosphates are said to form well-dispersed precipitates with hard waters, which are not adherent to fabrics; the latter are particularly effective with magnesium and iron,[105,108] but much less so with calcium. Tetrasodium pyrophosphate is a particularly desirable water softener.[109] It is capable of more or less completely eliminating magnesium hardness in water, through the formation of a soluble complex with magnesium ions, and is also, to some extent, similarly effective with calcium. It is now a more or less standard ingredient of the popular brands of packaged soap granules. Sodium hexametaphosphate is an even more effective water softener than tetrasodium pyrophosphate, particularly in waters high in calcium salts, but is rather expensive for ordinary use. Soiled clothes have a considerable free acidity, which is more economically neutralized by alkaline builders than by soap.

Salt is an essential material in soapmaking, but no significant amount ordinarily remains in the finished soap.

Certain compounds which may be incorporated into soaps are important from the standpoint of their antioxidant effect, or ability to stabilize the soap against rancidity. An excess of alkali of any kind appears to exercise some measure of antioxygenic activity. Sodium silicate is a well-known antioxidant. Sodium hyposulfite and sodium thiosulfate are sometimes added to soaps in small amounts purely for their antioxidant value. Stannous chloride is a powerful antioxidant and is also useful in white soaps as a bleaching agent. Rosin is to some degree an antioxidant. Most of the organic antioxidants which are effective in fats react with alkalies to form undesirable dark-colored compounds in soaps. However, many organic soap antioxidants have been patented.

Titanium dioxide is often incorporated in white milled soaps to improve the whiteness of the product, as is also zinc oxide. Siliceous materials are used as abrasive agents in scouring soaps and powders and mechanic's hand soaps.

Perfumes are an invariable ingredient of toilet soaps, and many of these soaps are also artificially colored. A considerable variety of other mate-

[104] R. C. Merrill, *J. Am. Oil Chem. Soc.*, *25*, 84-95 (1948).
[105] A. S. Richardson, *Ind. Eng. Chem.*, *15*, 241-243 (1923).
[106] F. D. Snell, *Ind. Eng. Chem.*, *25*, 162-167 (1933).
[107] J. Powney and R. W. Noad, *J. Textile Inst.*, *30*, 157-171T (1939).
[108] G. P. Vincent, *J. Phys. Chem.*, *31*, 1281-1315 (1927).
[109] J. Janota and H. H. Hull, *Oil & Soap*, *17*, 96-100 (1940).

rials are used to convey distinctive properties to special toilet soaps, including alcohol, sugar, pine tar oil, cresol, pyrethrum or derris extractives, sulfur, mercury salts, etc.

Organic solvents such as petroleum naphtha and cyclohexanol are sometimes added in minor amounts to laundry and industrial soaps for their solvent and dispersive action.

A highly interesting recent development has been the use of so-called optical bleaching agents in soaps.[109a] These consist of luminescent compounds which have the power of absorbing incident ultraviolet light and re-emitting it as visible light of longer wave length, i.e., as bluish light which tends to mask a yellowish tinge and give an appearance of enhanced whiteness to the soap, or to cotton fabrics washed in the soap, if the agent is cotton substantive. A popular brand of a packaged quick-dissolving product has contained an optical bleaching agent of the latter type for some time. The concentrations used are said to be of the order of 0.005–0.05%. A popular agent for enhancing the whiteness of soap bars is β-methylumbelliferone. Among the more effective cotton substantive agents are certain diaminostilbene and diphenylimidazolone derivatives.

TABLE 88

PRODUCTION OF SOAP IN UNITED STATES IN 1939 AND 1947[a]

Type	Production, million lbs.	
	1947	1939
Toilet soap, bars..................................	565.6	409.1
White laundry or household bars..................	406.6	660.7
Yellow laundry or household bars.................	358.3	578.8
Other bars..	28.1	—
Chips and flakes, packaged........................	228.0	284.3
Chips and flakes, bulk............................	195.1	134.3
Granulated, powdered, and sprayed, packaged.......	1412.5	892.7
Granulated, powdered, and sprayed, bulk..........	134.0	
Washing powder, packaged.........................	84.8	131.8
Washing powder, bulk.............................	106.3	110.4
Cleansers (abrasive), packaged....................	267.1	167
Cleansers, bulk...................................	77.2	19
Shaving cream (lather-type).......................	9.3	7.9
Shaving soap......................................	6.3	5.6
Liquid, packaged and bulk........................	16.7	42.8
Paste and jelly...................................	45.9	—

[a] U. S. Bureau of the Census, *Census of Manufactures*, 1947.

[109a] For a review of these agents, see A. Landbolt, *Am. Dyestuff Reptr.*, 38, 353 (1949. See also Lever Bros. and Unilever, Ltd., Brit. Pats. 567,716 and 568,810 (1945); 575,406, 584,436, and 584,484 (1947).

2. Production and Consumption

Data on the factory production of different types of soap in the United States in 1929 and in 1947 are recorded in Table 88. The period between these years has been marked by a continuing shift in preference from bar soaps to quick-dissolving forms for household use other than for toilet purposes. Since 1947 a very large increase in the consumption of packaged synthetic detergents has undoubtedly cut heavily into sales of quick-dissolving soaps.

3. Characteristics of Soaps Saponified by Different Methods

The full-boiled process is commonly used for saponifying fats, because it recovers the glycerol produced by saponification, and also produces pure and high-grade soaps. Properly carried out, this process gives a product completely free of unsaponified fat and containing less than 0.1% free alkali. In most soaps the free alkali, initially present as sodium hydroxide, is later more or less completely converted to sodium carbonate by absorption of carbon dioxide from the air during the drying operation. The settled soap resulting from full boiling consists substantially of about 63–67% combined with about 33–37% of water. It will contain a negligible amount of salt, and not more than about 0.5% glycerol. Since there is some segregation and removal of metallic soaps and other impurities in the niger phase in the boiling operation, soap made by the full-boiled process is lighter in color and purer than soap made from the same fat by other processes.

Potash soap cannot be salted out easily and separated from the glycerol produced by saponification as can sodium soaps, since the addition of sodium chloride to a potassium soap leads to a double decomposition with the formation of sodium soap and potassium chloride. Consequently, it is customary to prepare soft or potash soaps by the semiboiled process, in which the fat and alkali solution are simply weighed out in equivalent proportions and heated and mixed until saponification is effected. There is some production of sodium soap by this method, but it is not generally favored because it makes glycerol recovery impossible and also because of the generally inferior quality of the soap produced. It is difficult to adjust the proportions of alkali and fat so that there will be no substantial excess of either, or to obtain complete saponification of the fat even if the proportions are properly adjusted. Whereas the free alkali content of a good full-boiled soap will invariably be less than 0.1%, a semiboiled soap is generally considered satisfactory if it contains not over 0.3% free alkali. The possible presence of unsaponified fat and the lack of any separation of impurities in the niger makes soaps of this type relatively susceptible to oxidation, with attendant discoloration and development of rancid odors.

Sodium hyposulfite or other antioxidant is usually added to minimize this susceptibility. Semiboiled soaps of course retain all of the glycerol produced in the saponification process.

In the manufacture of soap by the cold process the fat and the alkali solution are mixed to form an emulsion at a relatively low temperature; the emulsion is run into frames, where saponification is completed. The characteristics of cold-made soaps are similar to those of semiboiled.

There is some production of soaps from fatty acids derived from the splitting of fats and oils. Much of this soap is derived from acidulated foots or other low-grade materials. In chemical composition soaps of this class are not substantially different from ordinary full-boiled soaps derived from a corresponding grade of fats, except that they contain no glycerol. However, their physical properties may be different; soaps made from fatty acids are said to be softer than soaps made by the direct saponification of fats, and to be distinctive in texture. It appears possible that the saponification of free fatty acids and the saponification of fats produce different microstructures in the finished soaps.

4. Effect of Different Factors on Physical Characteristics of Bar Soaps

The factor most profoundly influencing the physical characteristics of the finished soap bar is the chemical composition of the fat stock. The physical properties of comparable soaps from a number of individual fats and oils are summarized in Table 89. It will be seen that the hardness of the soap depends principally upon the degree of unsaturation (iodine value) of the fat, whereas the solubility depends, not only upon the unsaturation, but also to a large degree upon the average molecular weight of the fat. Coconut oil and palm kernel oil soaps are thus not only much the hardest soaps, but also among the most soluble. Above a minimum of about 0.7%, sodium chloride has a hardening effect on soaps.[110]

In general, soaps become increasingly soft with increasing moisture content, hence of the so-called full-boiled products, framed soaps containing 30–35% water are softer than milled soaps containing 12–15% water, with the newer continuously solidified soaps of about 20% water content occupying an intermediate position. However, the relationship between hardness and moisture content is complicated, as discussed previously (page 352), by the ability of soap to crystallize in different polymorphic forms, as well as by the influence of mechanical working and rates of cooling on the size and orientation of crystal fibers. Neat soap which is allowed to solidify relatively rapidly is harder than soap cooled more slowly.[110]

[110] J. L. Bowen and R. Thomas. *Trans. Faraday Soc.*, *31*, 164–184 (1935).

TABLE 89
PHYSICAL PROPERTIES OF FULL-BOILED SOAPS OF DIFFERENT INDIVIDUAL
FATS AND OILS[a]

| Oil | Titer, °C. | Hardness[b] | Solubility[c] | | Abrasion number[d] | | |
			100°F.	110°F.	60°F.	100°F.	110°F.
Coconut	23.4	20	10	8	3	40	54
Cotton	34.6	1.75	18	13	9	20	Melted
Hardened whale	31.0	2	23	19	9	16	20
Hardened whale	44.0	7	270	90	1	5	9
Olive, sulfur	16.0	3	8	6	14	Melted	Melted
Palm	45.0	5	190	60	4	6	10
Palm kernel	23.0	15	10	9	4	47	57
Peanut	23.0	1.25	21	14	12	Melted	Melted
Soybean	20.0	1.25	9	7	23	Melted	Melted
Tallow	43.9	3	195	65	7	7	12

[a] A. Rayner, *Soap, Perfumery & Cosmetics, 12*, 49, 152, 324 (1939).
[b] As measured by resistance to cutting wire.
[c] Time required for a small cube to dissolve in water, in a rotating cage.
[d] Relative loss in weight when rubbed mechanically in water under standard conditions (a measure of wastefulness in use).

5. TYPES OF COMMERCIAL SOAPS

(a) *Milled Toilet Soaps*

Toilet soaps of the more expensive grades are invariably of the milled type and are usually made from a full-boiled soap base. Milled soaps, which are produced from dried soap chips, worked and pressed into a coherent mass, are different in several respects from framed soaps, which are made by simply allowing the molten soap from the kettle to solidify in a large mass, which is later cut up into bars.

Framed and milled soaps differ considerably in moisture content. Although soap cakes of the framed type are dried to some extent in order to render them suitable for pressing, this drying occurs only upon the surface and does not reduce the moisture content of the soap greatly below the approximate 33% of the neat soap as it comes from the kettle. By drying the soap base in the form of very thin ribbons its moisture content may be readily reduced to 12 to 15%, which is that of most milled soaps. A further important difference between framed and milled soaps is in the crystal modification of the soap crystals in the two products. Framed soaps consist predominantly of soap in the so-called omega phase, whereas in milled soaps the beta phase predominates (see the preceding discussion of the physicochemical nature of soaps, Section C).

Since milled soap is less highly hydrated than soap solidified in the

frame, it might be expected that it would be correspondingly more difficult to dissolve, in washing operations. Such, however, is not the case, due to the readiness with which soap in the beta phase is penetrated by water. The penetration of water produces a layer of material upon the surface of the bar which, if not actually dissolved, is sufficiently softened to be readily removed and dispersed by mechanical action. The tendency of a cake of soap to absorb water at the surface is not desirable to an unlimited extent. If excessive, it produces a bar that is unpleasant to handle and wasteful to use. However, it does have the apparent effect of improving the solubility and lathering properties of the soap.

Since perfuming and coloring materials are incorporated into milled soaps while the latter are relatively cold, bars of this type may be much more readily perfumed than framed soaps. Milled bars may also be produced with a bright, polished, surface finish impossible to obtain by any other means of processing.

Milled soaps usually contain in the neighborhood of 20% of coconut oil or another oil of the lauric acid group. In the highest grade of white soaps the remainder of the oil usually consists of a light colored tallow, and in some cases, hydrogenated whale oil. In lower grades of white soap, or in colored soaps, palm oil or hydrogenated fish oils may partially or wholly replace the tallow. If the soap is to be colored, the soapmaker has a much wider variety of fats at his disposal than if it is to be white, since the colors added to the soap will mask the natural tints of highly colored or low-grade oils.

Good milled soaps do not contain more than 15% of water. They do not contain rosin, or any filling or building material other than perhaps a fractional percentage of titanium dioxide or other white pigment, and in addition to water consist substantially of pure soap. Their free alkali content should be less than 0.1%, calculated as NaOH. The glycerol content of such soaps is not generally greater than about 0.75%.

(b) Unmilled or Frame-Solidified Toilet Soaps

Although most of the bar toilet soap made in the United States is a milled product made from a full-boiled base, there is some manufacture of frame-solidified toilet soap, saponified by the cold or semiboiled processes. A good deal of this soap is made by small manufacturers, who favor these processes because they do not require expensive equipment or the services of an experienced soap boiler. However, most of the large soapmakers customarily manufacture a few types of unmilled toilet soap.

One of these types is Castile soap, which may be made wholly or largely from olive oil. Other toilet soaps which are customarily unmilled are usually made from coconut oil. They are popular in sections where the water is extremely hard, and for use with sea water, because of their ready lather-

ing properties. For use with soft water they are less desirable than soaps made from a blend of coconut oil with other fats. They are considered rather harsh in their action on the skin, partly because some of them are high in free alkali content (often as high as 0.5%) and partly because of their high content of C_{10} and C_{12} soaps, to which many people are sensitive.

Unmilled cold-made toilet soaps are quite variable in their moisture content, which may vary between about 25 and 45%. As noted above, they are often high in free alkali and usually contain in the order of 0.5–2.0% salt, sodium thiosulfate, sodium hyposulfite, etc., added as a preservative. They also contain varying percentages of glycerol. The cheaper grades are sometimes filled with sodium silicate or other alkalies.

Unmilled toilet soaps, and particularly those made by the cold process cannot be as delicately perfumed as milled soaps, because the perfuming materials must be added to the soap base while the latter is hot. In the case of cold-made soaps, any perfumes or colors used must be resistant to both heat and strong alkali. Unmilled soaps are therefore less well perfumed and less commonly colored than milled soaps.

(c) Special Bar Toilet Soaps

There are a number of more or less well-defined types of special toilet soap bars which may be distinguished from the standard bar soaps mentioned previously.

The so-called *transparent* or *glycerin soaps* depend for their distinctive appearance upon the fact that soap is deposited from alcoholic solution in a translucent, ultramicrocrystalline form.[111] Glycerol and sugars also tend to cause soap to assume this form. The effect is entirely physical, and depends upon the conditions under which the soap crystallizes rather than the presence of alcohol or any other substance in the finished soap cake. Thus, a transparent soap made with the aid of alcohol retains its appearance after most of the alcohol has been evaporated from it.

Transparent soaps vary greatly in composition. They may be prepared simply by dissolving soap flakes in alcohol and then driving off the greater part of the alcohol. Such a product will not be greatly different in composition from the original soap flakes. A more usual method of manufacture, however, is to add alcohol and glycerol, in the proportion of about two parts of alcohol to one of glycerol, to a hot saponified batch of semiboiled soap until a rapidly cooled sample is clear, after which the batch is framed in the usual way. Sugar may also be added. The fats used in transparent soaps usually are tallow and coconut oil. Up to about 30% castor oil is often used in the fat charge, as the presence of this oil reduces the amount of alcohol, glycerol or sugar required to render the soap trans-

111 J. W. McBain and S. Ross. *Oil & Soap, 21,* 97–98 (1944).

parent. The anhydrous soap content of transparent soaps is usually well under 50%.

Castile soap is made either from pure olive oil or a mixture of oils which in most cases approximate the fatty acid composition of olive oil, usually by the cold process. It is reputed to be less irritating to the skin than ordinary toilet soaps, and hence is in some demand as a medicinal soap and as a soap for infants, etc.

The mildness of Castile soap, in comparison with ordinary toilet soaps of good quality, is due to the fact that it contains none of the medium molecular weight fatty acids which are present in coconut or palm kernel oils and which are somewhat irritating to the average skin. The worst offenders in the way of skin irritation are said to be the soaps of capric and lauric acids; different individuals differ markedly in their reaction to these soaps. By employing an oil consisting largely of oleic acid in the manufacture of Castile soap it is possible to obtain quite good solubility in the product without the benefit of coconut oil. At the same time, the absence of a large proportion of linoleic or linolenic acid in the soap insures a fair stability toward oxidation.

There is very little *mottled soap* consumed in the United States, but there is some demand for this product in certain other countries. The blue streaks in a mottled soap, which are interspersed with a natural white or cream color, are due to the presence of a small amount (*ca.* 0.25%) of ultramarine blue added to the soap kettle before the soap is finished. By suitably finishing the soap in the presence of an excess of alkali, without separation of the niger, it may be charged to the frames in the form of two distinct but intermingled phases, one only of which contains the blue coloring material. The final appearance of the finished soap is developed by very slow cooling in the frames. Since the manufacture of a mottled soap in this fashion requires very careful control of the boiling process, mottled soaps are also prepared in some cases by careful hand mixing of a colored and an uncolored base.

Mottled soaps do not usually contain more than about 50% of anhydrous soap, and are high in free alkali. They are not usually made from fats of the highest grades and are often heavily filled with sodium silicate.

Superfatted soaps are produced in limited quantity for use by people with very dry skins or others who wish a soap containing an excess of fat rather than alkali. Superfatted soaps are less irritating than ordinary soaps to a very sensitive skin. The superfatting agent, which is usually added to the amount of about 1%, is generally lanolin, but may be olive oil, peanut oil, or any other oil or fat. Soaps of this type are prepared by incorporating the added fat in full-boiled soap before the latter is milled. Another special type of soap is made with an excess of alkali, consisting

usually of about 5% of soda ash, for use where there is excessive oiliness of the skin.

Carbolic or *carbolated* soaps do not usually contain carbolic acid or phenol but are made rather with the addition of a small percentage of commercial cresylic or tar acids. Although the original appeal of such soaps was through their possible disinfectant value, it is dubious whether this value is very high in the case of most products, and generally the phenolic constituents serve merely to impart a distinctive odor to an ordinary milled toilet soap. Carbolic soaps in the bar form are invariably colored, usually with a red dye. This type of soap is also manufactured in liquid form.

Pine tar soaps contain in the neighborhood of 5% of a special pine wood tar distillate which gives them a distinctive odor. Considerable amounts of this type of soap are sold in bar form, although its greatest popularity is as an ingredient for a liquid shampoo. Pine tar soaps have a distinctive black color.

Mechanic's hand soap is marketed in a bar form, although somewhat greater quantities of this item are consumed in the form of powders and pastes. This soap contains a large proportion, usually over 50% of pumice or other abrasive material, which is effective in removing deeply imbedded dirt or grease from the hands. Since it is low in its content of anhydrous soap, such soap as it does contain must lather freely, in order to make its over-all lathering properties comparable to those of an ordinary toilet soap. The base for a mechanic's hand soap is often a cold-made coconut oil soap filled with sodium silicate.

A great variety of *medicated soap* bars have appeared on the market from time to time. They usually consist of a milled product in which the medicament is worked into the soap in the milling operation. The agents which have been used in medicated soaps include mercuric iodide, sulfur, insecticides of the pyrethrum type (for animals), iodine, ichthyol, etc.

A recently introduced toilet soap containing hexachlorophene (*bis*-3,5,6-trichloro-2-hydroxyphenylmethane) as a bacteriostatic agent is said to be a *bona fide* deodorant soap.

(d) General Purpose Floating Soaps

Two of the popular brands of American bar soaps (Ivory and Swan) may be classed as general purpose soaps, inasmuch as they are widely used both as bath and toilet soaps and for general household cleaning. They are made from a pure neat soap which has been processed to reduce the moisture content to *ca.* 20%. The fat stock used usually contains a little more coconut oil than that for most milled soaps, and a small amount of potash soap is often present. They are not colored or highly perfumed, and

are solidified and extruded continuously by special processes which avoid the milling operation and yet produce large, relatively firm bars, with the soap substantially in the quick-dissolving "beta" phase (page 354). In the solidification process a sufficient amount of finely dispersed air is incorporated to reduce the specific gravity to about 0.8 and produce a bar that will float in water.

(e) Shaving Soaps and Creams

In shaving soaps, as in other toilet soaps, detergency is important. The shaving soap must remove the oily coating normally present on the beard so that the latter may become softened through the absorption of water. However, the lather produced by the soap also provides the absorbed water, so the lathering qualities are equally important. A good shaving soap or cream must dissolve readily, form a heavy, fine-grained, and abundant lather which will not break down or dry out during the shaving operation, and be free of any tendency to irritate the tender surfaces of the newly shaved face.

Shaving bars and sticks are usually made by the semiboiled or cold processes since a certain proportion of glycerol in the finished product is desirable, to prevent drying and for its effect on the quality of the lather. It is essential that shaving soaps contain no free alkali, either in the form of hydrate or carbonate. This is usually assured by superfatting the soap with 0.5 to 1.0% of stearic acid.

Since it is stearic acid soaps that produce the close, thick lather desirable in a shaving soap, there must be a high percentage of this constituent in the fatty materials used. Usually not less than one third of the total fats consist of commercial stearic acid. Coconut or palm kernel oil is also a customary ingredient, to the amount of 20 to 35% of the total fats. The remaining fat may be tallow, palm oil, olive oil, etc.

A sodium soap made to the approximate formula indicated above would be entirely too hard and insoluble, therefore it is necessary to conduct the saponification partly with caustic potash instead of caustic soda. The percentage of potash soap in the finished product will vary somewhat with the ratio of stearic acid to unsaturated or shorter chain saturated acids in the fat charge, but will not usually be less than half that of the sodium soap.

The production of shaving soap is much exceeded by that of shaving cream, which is packaged in collapsible tubes. Shaving creams vary somewhat in composition. Some consist merely of the potassium soaps of a mixture of relatively soft oils. However, in the type of shaving cream which is most popular in the United States, the ingredients are essentially

the same as those of shaving soap, with suitable changes in the proportions, to maintain the cream in a soft, plastic form, easily pressed from the tube and distributed on the bristles of the shaving brush and on the face.

In this type of shaving cream somewhat greater proportions of stearic acid are used than in shaving soaps, and correspondingly lesser amounts of coconut oil and tallow or similar fats. More caustic potash and less caustic soda is used and also more water. The product is also more heavily superfatted. Shaving creams usually contain about 35% anhydrous soap in the proportions of about 1 part sodium soap to 5 parts potassium soap. They contain in the neighborhood of 5% free fatty acids, which are usually generated in the soap by the addition of the proper amount of sulfuric, hydrochloric or boric acids. The presence of a large percentage of free stearic acid in the cream is responsible for its distinctive sheen, and also is said to contribute in an important way to the soft body of the product.

The latherless or "brushless" shaving creams, which have recently become popular, are essentially oil-in-water emulsions similar to vanishing creams. The oil in these creams is usually mineral oil, although a vegetable oil may be used. Surface-active materials are incorporated, to stabilize the emulsion and to assist in wetting the beard so that it will readily absorb water. A considerable variety of surface-active agents is used in the different preparations. In one type of cream the aqueous phase consists of a paste of superfatted potassium soap largely made from stearic acid. In another type the potassium stearate is replaced with triethanolamine soaps. Still others employ sulfonated tallow or other sulfonated oils. All types contain the maximum amount of water consistent with the proper body in the product, i.e., about 70 to 80%.

(f) Powdered Soaps

Powdered soaps are used in considerable quantities in dentifrices and miscellaneous toilet preparations. Most powdered soap is a tallow–coconut oil product, saponified by the full-boiled process and then flaked, dried to a near-anhydrous condition, and ground. Such soap is not made by the cold or semiboiled processes because the presence of glycerol makes the grinding difficult. Soaps made by these processes are also less stable than full-boiled soaps. Stability is highly important in this product, because of the surface exposed to oxidation.

Powdered soap intended for use in dentifrices is usually made of the very highest grade materials, in order to minimize taste or odor. Since the soaps of the low molecular weight fatty acids of coconut oil have a slight soapy taste, a full-boiled soap of the Castile type is preferred by some users although it is less stable toward oxidation than soap containing coconut oil.

(g) Shampoos

Liquid shampoos are used in large quantities in the home and in barber and beauty shops for washing the hair. The principal requirements in a shampoo are an ability to produce a profuse but light lather and to rinse readily from the hair. These requirements are best met by a soap containing a large proportion of coconut oil. Many liquid shampoos are simply solutions of potash coconut oil soap, although some contain a minor proportion of soap derived from olive oil or other soft oil. Coconut oil soap also has the advantage of being very soluble and hence unlikely to jell in the bottle at low temperatures.

The usual percentage of real soap in a liquid shampoo is about 20–25%. When a shampoo is made up to this strength it will usually show some tendency to cloud at low temperatures, because of the separation of small amounts of stearic and other fatty acid soaps of high molecular weight. As the trade demands an absolutely clear, sparkling product, it is necessary to employ a winterizing treatment, in which the solution is chilled and held at a low temperature for a somewhat prolonged period before it is filtered and bottled.

Since any variety of soap tends to deposit insoluble calcium and magnesium salts from ordinary waters, and since these are very detrimental to the appearance of the hair, nonsoap detergents are quite widely used in shampoos. The materials formerly used for this purpose consisted chiefly of sulfonated olive and castor oils, but these have now largely been supplanted by such synthetics as the ethanolamine salts of sulfated alcohols or monoglycerides from coconut oil.

(h) Bar Laundry Soaps

The materials known as laundry soaps are not used in commercial laundries, but are employed in the household for laundry, dishwashing, and general cleaning. Household soaps in bar form are not as popular now as they were formerly, due to the introduction of many brands of packaged flakes, granules, beads, etc., but are still produced and consumed in very large quantities.

The two principal varieties of laundry soap are white and yellow. *White laundry soap* is usually a full-boiled product made from 25–40% coconut oil and 60–75% tallow, hydrogenated fish oil, etc. It is always prepared with sodium silicate or other soap builder, in sufficient amount to reduce its anhydrous soap content to somewhat less than 50%, and is never milled.

Yellow laundry soap is similar to white laundry soap except that it contains a substantial proportion of rosin. The rosin imparts to the bar a dis-

tinctive yellow color. Rosin soap is relatively soft and sticky, hence yellow soaps cannot be prepared with as much builder as white soaps. Their anhydrous soap content is usually over 50%. It is also usual to employ less coconut oil in yellow than in white laundry soap, because of the relatively high solubility of rosin soap.

Naphtha soap usually consists of a white laundry soap, to which has been added a small percentage of petroleum naphtha. The naphtha volatilizes from the soap quite readily, hence the amount in the finished bar, as it is delivered to the consumer, is quite variable. In the United States a soap cannot legally be sold as a "naphtha soap" unless it contains at least 1% of the hydrocarbon. In a concentration approaching the lower legal limit, the naphtha is of doubtful value in reinforcing the detergent action of the soap.

Marine or *salt water soaps* are principally used for laundry purposes on board ships. Because of the lesser susceptibility of the lower fatty acid soaps to "salt out," salt water soaps have in the past almost invariably been made from coconut oil.

(i) Soap Flakes, Granules, Etc.

In late years soap flakes, granules, and other quick-dissolving forms of soap have to a considerable extent replaced bar laundry soap for dishwashing, laundry work, and general household cleaning (see Table 88).

The quick-dissolving soaps are divided into two distinct classes, namely those consisting of pure soap, and those to which an alkaline builder has been added. The former are a relatively high-priced product and find their chief use in dishwashing and the home laundering of silks, woolens, and other fine articles of clothing. The products which contain builders are primarily general purpose home laundry soaps.

Soap chips or flakes are produced by chilling the molten soap in a thin sheet and then drying and breaking or cutting up the solidified sheet. Beads and granules are produced by spray drying. Beads are distinguished from granules by having the form of hollow rather than solid spheres. Thus their apparent density is very low. Both pure soap and builded soap are produced in all the various quick-dissolving forms, with one important exception: the so-called polished flakes, which are given a special milling treatment to improve their smoothness and luster, are invariably a pure soap product. These flakes are among the most expensive of the packaged soaps. They are invariably white, and are made from a base containing a considerable percentage of coconut or other lauric acid oil in combination with well-bleached tallow or other hard, light colored fat. Thus they are not different in composition from the high-grade floating soaps except in

moisture content, and may in fact be considered the quick-dissolving counterpart of the latter.

The flakes, chips, granules, etc., which are packaged for household use may be made from a variety of fats, but they usually contain coconut oil or similar oil when such oil is available, for the sake of the solubility and quick-lathering properties which it confers. High solubility and quick suds formation are particularly important in the pure soap products, since these are much used in cold or lukewarm water. In addition to the flakes and chips sold in household packages there is a large consumption of bulk chips, chiefly by commercial laundries. Bulk chips usually consist of pure tallow soap.

The quick-dissolving soaps contain much less moisture than bar soaps, since with a high water content they tend to cake in the package. Pure soap flakes, in particular, are extremely low in moisture, containing usually less than 5%. Granules and beads may contain 10% to 15% water. The percentage of builder incorporated in quick-dissolving builded soaps is quite variable, but is usually not less than about 15%. Formerly, the builders employed were principally soda ash and sodium silicate. Recently, however, these have been largely replaced by various polyphosphates.

A recent novel development in the field of granulated household laundry soaps is the incorporation of a fluorescent dye with a high affinity for cotton fibers (see page 372). Traces of the dye remaining on white fabrics after rinsing and drying have sufficient fluorescence in daylight to give an appearance of enhanced whiteness.

(j) Washing Powders

Washing powders are relatively cheap detergents consisting of a small proportion of soap mixed with a large proportion of soda ash or other alkaline material. The amount of real soap in these powders is quite variable, but is in general much less than 50% and often not greater than 10% to 20%. Although the standard alkaline ingredient for washing powders is soda ash, trisodium phosphate, or other builders are sometimes used.

Washing powders are principally made by pulverizing the mixed and dried product in various types of mills, although recently there has been a tendency to adopt the method of spray drying for washing powders.

The consumption of this material is about equally divided between household and bulk users. The use of washing powders in the household appears to have somewhat declined recently; this is probably due to the increased popularity of builded granulated soaps.

(k) Scouring Soaps and Cleansers

Scouring soap cakes are compounded from a finely ground siliceous material with only sufficient soap and soap builder to hold the cake together. The usual proportions are about 80% abrasive and approximately 10% each of soda ash or other alkaline builder and soap. The soap usually contains a sufficient amount of coconut oil to produce an appreciable lather. These soaps are chiefly used for cleaning and polishing windows, display cases and similar smooth, highly polished surfaces.

The cake form of scouring soap is much less popular than powdered scouring soaps or cleansers, which are widely distributed, both in household packages and in bulk. Cleansers are more or less similar in composition to cake scouring soaps, except that they contain less soap and the soap is usually made from lower grade fats. A popular brand at one time contained 2% anhydrous soap, 4% soda ash, 7.5% trisodium phosphate, and about 78% silica. The remainder consists of combined water. Cleansers are much used in the household for cleaning kitchen utensils, bath tubs, sinks, etc.

Recently, there has been a considerable use of alkyl aryl sulfonates as a replacement for soap in scouring powders.

(l) Liquid Soaps

Liquid toilet soaps find their principal use in public wash rooms, since they are easily dispensed from automatic or semiautomatic devices. They consist of aqueous solutions of soap made from potash and coconut oil or other lauric acid oil, mixed with a soft oil such as cottonseed, soybean, or peanut oil. The concentrated base is usually diluted for use to a soap content of about 15%. Liquid toilet soaps are not essentially very different from liquid shampoos, except that they are commonly made from lower grade oils, are not perfumed and are not as carefully clarified. The principal object in preparing a liquid toilet soap is to produce a solution which will not clog the dispenser, and which will form a satisfactory lather in the amount customarily discharged into the hand.

Liquid floor soaps are made in considerable quantities for washing linoleum, tile, and composition floors in offices, schools, institutions, and various public buildings. These soaps usually contain about 25% anhydrous soap, which is usually a superfatted soap of linseed or soybean oil. They are often compounded with a small percentage of pine oil. In the washing of floors it is particularly necessary that no alkaline residue be left after the floor is washed and rinsed. Such a residue is unsightly and is also injurious to paint or linoleum surfaces. By using a superfatted soap

it can be assured that any residue will be oily rather than alkaline. If the residue consists of a drying oil it will oxidize to produce a nonoily protective coating.

(m) Miscellaneous Industrial Soaps

A special class of soaps is manufactured for use in the organic solvents employed in dry-cleaning operations. Dry cleaners' soaps are usually potash products containing an excess of 5–10% of free fatty acids, most of which consists of oleic acid. In other dry cleaners' soaps, triethanolamine is used instead of caustic potash as the saponifying alkali. Triethanolamine soaps are freely soluble in dry cleaner's solvents, as well as in water. Obviously no large percentage of water can be tolerated in this class of soaps, hence saponification is carried out in the medium of an organic solvent, and the soap is marketed in the form of a solvent–soap paste or liquid containing 10–15% actual soap.

Automobile soaps are usually superfatted potash soaps made from linseed, corn, or soybean oils. Except for the fact that they are usually sold in paste rather than liquid form, they are similar to linoleum floor soaps.

A number of special soaps are made for scouring and cleaning operations in the manufacture of textiles. Although requirements for textile soaps are not exacting insofar as color, odor, etc., are concerned, and these soaps are usually made with cheap fats, some care is nevertheless required in their manufacture. In general, textile soaps must be free from builders and must be soluble at reasonably low temperatures, since textile fibers, particularly silk and wool, are injured by contact with alkalies at high temperatures. Relatively little tallow or coconut oil is used in making textile soaps; the principal fats used for the purpose are olive oil or olive oil foots, palm oil, corn, cottonseed, and peanut oil foots, distilled fatty acids, and greases. Most of the textile soaps are sodium soaps. The cold, semiboiled, and full-boiled processes are all employed in their manufacture.

Insecticide soaps are almost invariably made from caustic potash and one of the fish oils. Wire-drawing soaps consist of ordinary tallow or grease soaps containing added talc. The soap employed as an emulsifying agent in the copolymerization of butadiene and styrene to make synthetic rubber must be substantially free of linoleic or linolenic acids, as polyunsaturated acids retard polymerization.[112] The preferred material, therefore, is a chip soap product made from a slightly hydrogenated tallow.

[112] J. W. Wilson and E. S. Pfau. Ind. Eng. Chem.. 40. 530–534 (1948). W. C. Ault, B. A. Brice, M. L. Swain, B. B. Schaeffer, and M. J. Copley, J. Am. Oil Chem. Soc., 26, 700–704 (1949).

E. Surface-Active Agents Other Than Soap

Ordinary sodium or potassium soaps, used under the proper conditions, are generally the best available detergents and wetting agents. However, they have two disadvantages which limit their usefulness, particularly in industrial applications. One of these is their ease of hydrolysis, which makes them unsuitable for use in solutions of low pH; the other is their characteristic of forming insoluble soaps with the calcium and magnesium compounds which are found in varying amounts in almost all natural waters. Calcium and magnesium soaps are particularly troublesome in the washing of fabrics, inasmuch as they form coarse and greasy curds which tend to deposit upon animal or vegetable fibers.

Most of the so-called synthetic detergents and wetting agents have been developed with the object of overcoming the objectionable characteristics of soaps. In addition, a considerable amount of effort has been expended in developing materials for special uses which are not well served by soaps or compounds of closely similar structure, particularly as emulsifying agents and oil-soluble surface-active agents.

In the manufacture of synthetic detergents and other surface-active agents, unlike the manufacture of soap, there is very little use of inedible tallows and greases. Coconut oil is the most important raw material, and is supplemented largely by "soft" oils high in oleic acid.

A recent significant development, given impetus originally by the shortage of fats and oils during World War II, has been the introduction and acceptance on a very wide scale of a number of brands of granulated synthetic detergents for household dishwashing and laundry. Synthetic detergents, of a relatively expensive type, have been available in household packages for a number of years, but it is only recently that synthetics have achieved wide popularity except in areas which have very hard waters.

1. Structural Considerations

Soaps have the formula:

$$R.COO.Na$$
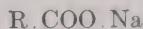
or in the ionized form in solution:

$$R.COO^- \qquad Na^+$$

where R represents a long chain aliphatic radical. The basic shortcomings of soaps, as set forth above, arise from an insufficiency of hydrophilic properties in the group, —COO. A method long recognized as effective for making the anion more hydrophilic is to introduce the sulfate group, —OSO$_2$O, or the sulfonate group, —SO$_2$O, either in place of the —COO

group, or at another place in the molecule. In the common "sulfonated" oils, the sulfate group is added at the double bond of oleic or other unsaturated acid or at the hydroxyl group of ricinoleic acid:

$$
\begin{array}{c}
OSO_2O \\
| \\
R.COO.X
\end{array}
$$
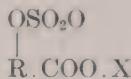
In the more recently developed and much more useful alkyl sulfates it replaces the —COO group:

$$R.OSO_2O$$
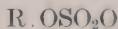
Sulfation or sulfonation is readily effected wherever a free hydroxyl group is present, e.g., in a fatty alcohol:

$$R.OH + H_2SO_4 \longrightarrow R.OSO_2OH + H_2O$$

Neutralization of the resulting sulfuric half-ester with sodium hydroxide produces sodium alkyl sulfate:

$$R.OSO_2OH + NaOH \longrightarrow R.OSO_2ONa + H_2O$$

In solution:

$$R.SO_2ONa \rightleftharpoons R.SO_2O^- + Na^+$$
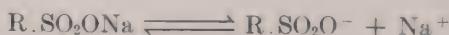
It is not always easy to produce a hydroxyl group joined directly to the carbon atom at the end of an aliphatic chain as in the fatty alcohol above; hence in many surface-active compounds union is effected through an intermediate linkage. The most common intermediates are an *ester linkage* through the partial ester of a polyhydroxy alcohol:

$$R.COOH + HO.X.OH \longrightarrow R.COO.X.OH + H_2O$$

and an *amide linkage* through an aminohydroxy compound:

$$R.COOH + H_2N.X.OH \longrightarrow R.CO.HN.X.OH + H_2O$$
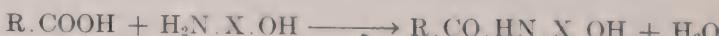
The lipophilic group in surface-active compounds is by no means restricted to a single straight chain. There may be two chains instead of one, and an aromatic radical may substitute wholly or in part for a straight chain. In mixed aliphatic-aromatic chains it is the total chain length rather than the number of carbon atoms that is important; one benzene ring is equivalent to approximately 3.5 aliphatic carbon atoms.[113]

Although the sulfate and sulfonate groups are the most common hydrophilic groups, others, such as the phosphate, are occasionally employed. A means for introducing hydrophilic groups which has recently found much favor, particularly in the production of nonionic surface-active agents,

[113] R. G. Paquette, E. C. Lingafelter, and H. V. Tartar. *J. Am. Chem. Soc.*, 65, 686–692 (1943).

involves the reaction of a long chain compound containing a free hydroxyl group with ethylene oxide:

$$R.OH + n\,C_2H_4O \longrightarrow R(OC_2H_4)_nOH$$
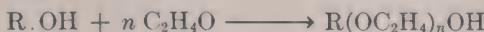
By this means, any number of hydrophilic OC_2H_4 groups may be added, and the product may or may not be sulfated, thus producing any desired ratio of hydrophilic to lipophilic properties in the molecule.

2. The Three Classes of Surface-Active Compounds

The preceding discussion has referred only to *anionic* surface-active agents, *i.e.*, to compounds which produce long chain or surface-active ions which are negatively charged. There is also an important class of *cationic* compounds, in which the charges of the ions are reversed:

$$R.NH_3^+ \qquad Cl^-$$
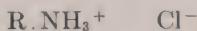
Most of the useful cationic agents are essentially of the structure shown above. However, the three hydrogen atoms are usually substituted with aliphatic or aromatic radicals of low molecular weight; a chloride or bromide ion is usually the anion.

A third class of surface-active agents of very rapidly growing importance consists of compounds which are *nonionic* in nature. In these the hydrophilic portion of the molecule is made up of hydroxyl or ether groups which are not ion-forming in solution. Monoglycerides and other partial esters of polyhydric alcohols are oil-soluble members of this class. By incorporating in the molecule a compound with a multiplicity of hydroxyl groups, such as a polyglycerol, some degree of water solubility can be achieved, but the most useful method of enhancing water solubility is by introducing a number of ethylene ether groups through reaction with ethylene oxide as described above.

3. Types, Brands, and Forms

Even a cursory treatment of all of the multitude of synthetic materials that have been produced and marketed is quite beyond the limitations of this volume. Reference will be made, therefore, to but a few of the more important types. For detailed information on specific products, as well as the general chemistry and technology of this complex and rapidly expanding field, the reader should consult the recent comprehensive treatises of Schwartz and Perry[114] and Sisley.[115] The trade names of commercial products are so frequently changed, and new products are being introduced at such a rapid rate, that it is difficult to maintain a

[114] A. M. Schwartz and J. W. Perry, *Surface Active Agents*, Interscience, New York, 1949.
[115] J. P. Sisley, *Index des Huiles Sulfonées et Détergents Modernes*, Teintex, Paris, 1949.

current list of those that are available. No attempt will be made here to give anything resembling a systematic listing of trade names. In the case of most of the representative types or members mentioned, essentially similar products are available under different names from a number of different manufacturers.

Although purified materials are also produced for special uses, much of the total production of the more common ionic surface-active agents consists of 30–40% of active material mixed with 60–70% of sodium sulfate or other inorganic salt which is usually a by-product of neutralization following sulfation or sulfonation. Most products are spray-dried or solidified and marketed in a granulated form, although there are also paste and liquid preparations. Packaged synthetic detergents for household use of the so-called "heavy-duty" type are usually compounded with a polyphosphate builder. There is virtually no production in a form resembling the familiar soap bar.

Most of the anionic agents are in the form of sodium salts, although there is some production of ammonium and ethanolamine salts, particularly for use in shampoos and other cosmetics.

4. PRODUCTION AND CONSUMPTION

A tremendous increase in the production and consumption of synthetic detergents, particularly for household use, has been one of the dramatic industrial developments following World War II. Accurate production figures for this period are not available, but it has been estimated[115a] that a production of 281 million pounds in 1948 increased to 531 million pounds in 1949 and 1,090 million pounds in 1950. These figures apply to the finished products, containing large proportions of inorganic salts and builders, and not to the active ingredient. The recent increased effectiveness and enhanced popularity of packaged household products has been in considerable measure due to the availability of tripolyphosphate and other polyphosphates and the general practice of incorporating these materials as builders.

5. ANIONIC COMPOUNDS

(a) Sulfated Oils

Sulfated oils are the oldest of the nonsoap surface-active agents, having been used in the textile industry for over a century. These oils are commonly termed "sulfonated oils," but technically speaking the term is a misnomer. The compounds chiefly resulting from "sulfonation" are sulfates, as represented by the grouping, $-CH_2.O.SO_2OH$. Sulfonates, which contain a direct carbon-to-sulfur linkage, $-CH_2.SO_2OH$, are pro-

[115a] F. D. Snell, *Chem. & Eng. News*, **29**, 36–38 (1951).

duced in only very minor amounts. In discussing surface-active agents it is necessary to make a distinction between the two classes of compounds, since in many cases the properties of sulfates and the corresponding sulfonates are quite different.

Oils are sulfated by treatment at a low temperature with strong sulfuric acid, with subsequent washing and neutralization of the sulfated mass. In castor oil sulfation appears to take place chiefly at the hydroxyl group of ricinoleic acid:

$$-CH_2CHOHCH_2- + H_2SO_4 \longrightarrow -CH_2CH.O.SO_2OHCH_2- + H_2O$$

$$-CH_2CH.O.SO_2OHCH_2- + NaOH \longrightarrow -CH_2CH.O.SO_2ONaCH_2- + H_2O$$
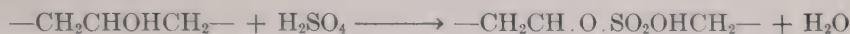
In ordinary fats and oils sulfation occurs at the double bonds of the fatty acids:

$$-CH_2CH:CHCH_2- + H_2SO_4 \longrightarrow -CH_2CH_2CH.O.SO_2OHCH_2-$$

$$-CH_2CH_2CH.O.SO_2OHCH_2- + NaOH \longrightarrow$$
$$-CH_2CH_2CH.O.SO_2ONaCH_2- + H_2O$$
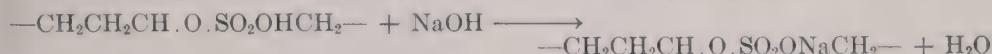
The fatty acids of the oil are sulfated more or less preferentially, according to their degree of unsaturation.

There are a number of side reactions, so that commercial sulfated oils consist of a complex mixture containing many substances other than sulfated glycerides and other glycerides which may have escaped sulfation. There is in particular a large production of free fatty acids, from hydrolysis of the glycerides; some of the free acids are of course also sulfated. This hydrolysis is accompanied by partial conversion of the neutral oil to mono- and diglycerides. There is a minor production of sulfonic acids:

$$-CH_2CH:CHCH_2- + H_2SO_4 \longrightarrow -CH_2CHOHCH.SO_2OHCH_2-$$

In the sulfation process itself and also during washing and neutralization there is some degree of hydrolysis of the fatty acid sulfates, to form hydroxy acids:

$$-CH_2CH.O.SO_2OHCH_2- + H_2O \longrightarrow -CH_2CHOHCH_2- + H_2SO_4$$

The hydroxy acids are quite reactive under the conditions of sulfation and may undergo condensations to form lactones, lactides, and estolides.[116] Estolides are probably also formed by the direct reaction of fatty acids and fatty acid sulfates. In some oils, particularly highly unsaturated fish oils, there is oxidation of the unsaturated fatty acids, accompanied by polymerization of the products of oxidation. Iso-oleic acid has been found in sulfonated oils,[117] and it is probable that there is other fatty acid isomerization during the reaction.

[116] D. Burton and G. F. Robertshaw, *Sulphated Oils and Allied Products*. Chemical Pub. Co., New York, 1942.
[117] R. M. Koppenhoefer, *J. Am. Leather Chem. Assoc.*, *34*, 622–639 (1939).

Since sulfation occurs more readily at the hydroxyl group of ricinoleic acid than at the double bonds of unsaturated fatty acids, the sulfation of castor oil (to produce the Turkey red oil of commerce) proceeds with less extensive side reactions than does that of other oils. The complete characterization of sulfated oils is naturally a matter of extreme difficulty, but it is possible to separate samples roughly into neutral or unreacted oil, unreacted fatty acids, and sulfated material, by proper procedures, and to judge the degree of sulfation of the latter so-called sulfo oil. Analyses of typical samples of commercial oils, as reported by Koppenhoefer,[117] are given in Table 90.

TABLE 90

ANALYSES OF COMMERCIAL SULFATED OILS OF MEDIUM DEGREE OF SULFATION[a]

Analysis	Castor oil	Neatsfoot oil	Cod oil
Water, %................................	28.6	3.75	25.6
Ash, %..................................	7.72	3.33	5.94
Combined SO_3, %.......................	4.95	3.01	3.50
As sulfo acids, %.....................	24.3	14.2	16.5
Acid value............................	35.6	100.9	59.6
As free fatty acids, %................	18.9	50.7	33.0
Total fatty matter, %.................	62.3	88.4	67.6
Calculated composition of fatty matter:			
Sulfo oil, %..........................	36.3	15.6	23.2
Free fatty acids, %...................	28.1	55.6	46.4
Neutral oil, %........................	35.6	28.8	30.4

[a] According to R. M. Koppenhoefer, *J. Am. Leather Chem. Assoc.*, *34*, 622–639 (1939).

Obviously a single oil may yield sulfated products of widely different characteristics, according to the extent to which sulfation is carried and to which side reactions are permitted to take place. The sulfation process is generally varied to fit the requirements for the finished product. For some purposes, as in textile finishing, it may be desirable for the sulfated oil to form a completely clear solution in water. In other applications, of which the fat liquoring of leather is an example, it is only necessary for the sulfate oil to form an emulsion with water.

As surface-active agents, sulfated oils have the advantage over soaps of being effective in acid solution. Also they are less sensitive to hard waters, although they are still capable of forming relatively insoluble calcium and magnesium salts. They are somewhat inclined to hydrolyze, with the liberation of sulfuric acid, in aqueous solution, and are quite heat-labile in the presence of water. Although they are classed as the most satisfactory surface-active agents for certain specific purposes, they are less versatile wetting, deflocculating, and emulsifying agents than most of the newer materials. They are not good detergents.

Sulfated oils are employed in a variety of industries. Among their more important uses are as textile lubricants and as assistants in the dyeing of textiles (castor oil, olive oil, etc.) and as fat liquoring materials for leather manufacture (neatsfoot oil, fish oils).

The amounts of the different fats and oils sulfated in the United States in 1943 are shown in Table 91.

TABLE 91

OILS SUBJECTED TO SULFONATION IN UNITED STATES IN 1943[a]

Oil	Quantity, 1000 lbs.
Cottonseed	272
Peanut	2,218
Corn	1,318
Soybean	1,904
Castor	6,586
Coconut	18
Olive and olive oil foots	52
Rapeseed	4
Palm	1
Linseed	67
Other vegetable oils	1,767
Tallow	5,723
Neatsfoot oil	2,041
Cod oil	2,146
Other liver oil	90
Marine mammal oil	776
Fish oil	8,975
Grease (other than wool grease)	248
Wool grease	318
Total	*34,524*

[a] U. S. Bur. Census reports.

(b) Alkyl Sulfates

Sodium alkyl sulfates are prepared by reducing fatty acids to the corresponding fatty alcohols by sodium reduction or catalytic hydrogenation, sulfating the alcohols, and converting the resulting alkyl sulfuric acid to the sodium salt with sodium carbonate or other alkali. Thus these compounds are structurally similar to soap, except that the —COONa group of soap has been replaced with —OSO$_2$ONa:

$$CH_3(CH_2)_{10}COONa$$
Sodium laurate

$$CH_3(CH_2)_{11}OSO_2ONa$$
Sodium lauryl sulfate
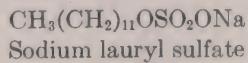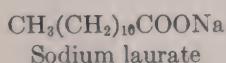
These compounds are highly efficient detergents and wetting agents, and do not form insoluble calcium and magnesium compounds with hard waters. Unlike soaps, they are stable and effective in n___ ___ slightly

acid solutions, although they are hydrolyzed in hot, strongly acid solution. The considerable amount of residual sodium sulfate in most commercial products is considered to improve their action, including their resistance to hydrolysis by acids.[118]

Commercial preparations of sodium alkyl sulfates are made from mixed fatty acids, such as those derived from coconut oil, and are also available in forms consisting substantially of a single fatty acid, as sodium lauryl sulfate, sodium oleyl sulfate, or sodium stearyl sulfate. Any alkali can of course be used to neutralize the alkyl sulfuric acid. Triethanolamine alkyl sulfates are prepared commercially for certain purposes.

Alkyl sulfates are among the oldest synthetic detergents, having been produced in Germany as early as 1930, and are best known as Gardinols, the trade name under which they were first marketed in this country. Present trade names include Orvus, Duponol, and (for household use) Dreft and Drene. Tergitol 08 is a product of the alcohol 2-ethylhexanol, which is not derived from fats.

The alkyl sulfates are used principally as detergents, in a very wide variety of applications.

(c) Alkyl Ester Sulfates

The most important ester-linked surface-active agents employ glycerol as the polyhydric alcohol bridging between lipophilic and hydrophilic groups:

$$
\begin{array}{l}
R-C- \\
\quad -C-OSO_2ONa \\
\quad -C-OH
\end{array}
$$
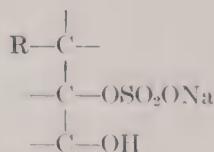
They are manufactured by sulfating monoglycerides, which are simply and easily prepared (page 819) (though less easily separated from other products of reaction with glycerol), and must be considered, potentially at least, as among the cheaper types of synthetic detergent. Although not highly stable to either acids or alkalies, they are unaffected by hard waters, and are excellent for most cleaning purposes. Commercial products are Arctic Syntex M and L and (for retail) Vel and Halo.

(d) Alkyl Amide Sulfates

A fairly popular class of surface-active agents employs an amide linkage between the alkyl radical and a sulfate group:

$$R.CONHC_2H_4.OSO_2ONa$$

[118] G. _____ Inds. corps gras., 1, 136–139 (1945).
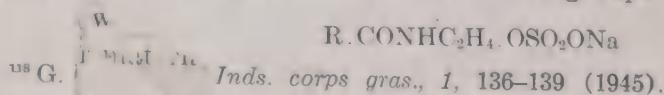
They are made by reacting fatty acids with monoethanolamine and sulfating and neutralizing the reaction product. The reaction is simple and easily carried out, and the better products are good foaming agents and detergents, although the less carefully made commercial products are said[114] to be inferior because of the presence of unsulfatable esters, which may detract markedly from the surface-active properties.

The products marketed under the trade names of Sulframine DR and Miranol SR are representative of this class.

(e) Alkyl Sulfonates

Compounds comparable to the sulfated fatty alcohols, but containing the sulfonate rather than the sulfate group:

$$R.SO_2ONa$$
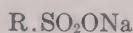
have been the subject of a great deal of scientific study (see, for example, page 357), but have never been used commercially as surface-active agents, because of their difficulty of preparation and the insolubility of their calcium soaps.[119]

Long chain saturated hydrocarbons from petroleum can be converted to alkane sulfonyl chlorides, $R.SO_2Cl$, by reaction with sulfur dioxide and chlorine under the proper conditions. The sulfonyl chlorides are then easily converted to sulfonates, which are satisfactory lime-resistant detergents. In these products the long chain radical is of course not attached at the end of the chain to form the normal primary aliphatic compound indicated in the preceding paragraph. One of the popular surface-active agents of this class is marketed under the trade name MP-189.

(f) Alkyl Ester Sulfonates

One of the oldest synthetic surface-active agents, Igepon A or AP, utilizes an ester linkage, and is made by reacting the chloride of commercial oleic acid or other fatty acid chloride with the sodium salt of isethionic acid:

$$CH_3(CH_2)_7CH:CH(CH_2)_7COCl \quad + \quad HO(CH_2)_2SO_2ONa \longrightarrow$$

Oleoyl chloride   Sodium salt of
                                isethionic acid

$$CH_3(CH_2)_7CH:CH(CH_2)_7CO.O(CH_2)_2SO_2ONa \quad + \quad HCl$$
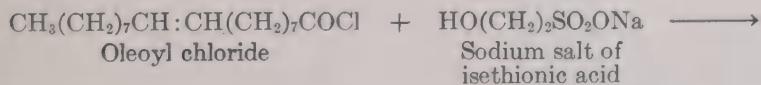
Igepon A is an effective lime-resistant detergent and general purpose surface-active agent, but like other esterified products, is not stable in hot alkaline solution.

A number of surface-active sulfoacetates have been described in the literature. One of these, monostearin sodium sulfoacetate:

[119] R. M. Reed and H. V. Tartar, J. Am. Chem. Soc., 58, 32   5).

$$-C-OOC(CH_2)_{16}CH_3$$
$$-C-OH$$
$$-C-OOC.CH_2.SO_2ONa$$
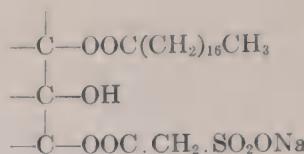
has been widely used under the trade name of Emargol as an emulsifying and antispattering agent for margarine.

Properly classed with this group of surface-active agents are the dialkyl sulfosuccinates, *e.g.*, diamyl sodium sulfosuccinate:

$$CH_3(CH_2)_4O.CO.CH_2$$
$$CH_3(CH_2)_4O.CO.C.SO_2ONa$$
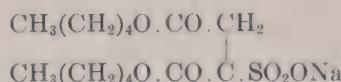
The alkyl groups in these compounds must be relatively short if the latter are to have satisfactory solubility; hence they are not commonly derived from fatty acids. Under the trade name of Aerosols they are known as extremely effective wetting agents. Their double chain structure is considered[120] to contribute to their great effectiveness in low concentrations.

A related wetting agent, Nekal NS, has three alkyl groups:

$$CH_3(CH_2)_5O.CO.CH_2$$
$$CH_3(CH_2)_5O.CO.C.SO_2.O.Na$$
$$CH_3(CH_2)_5O.CO.CH_2$$
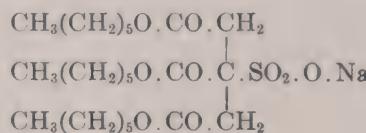
(g) Alkyl Amide Sulfonates

Another old, highly effective, and popular detergent and general purpose surface-active agent, Igepon T, has an amide linkage, produced by condensing oleic acid chloride with the sodium salt of taurine or methyltaurine:

$$CH_3(CH_2)_7CH:CH(CH_2)_7COCl + NH_2(CH_2)_2SO_2ONa + NaOH \longrightarrow$$
Oleoyl chloride   Sodium salt of taurine

$$CH_3(CH_2)_7CH:CH(CH_2)_7CO.NH(CH_2)_2SO_2ONa + H_2O + NaCl$$
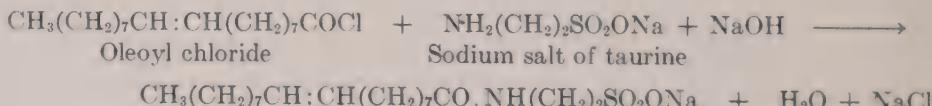
The methyl taurine product is said to be the better detergent.

Igepon T is more resistant to alkalies and generally more satisfactory than the ester-linked Igepon A.

The commercial preparation of Igepon T has recently been described in detail by Kastens and Ayo.[120a]

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[120] See G. S. Hartley, *Trans. Faraday Soc.*, 37. 130–133 (1941).
[120a] M. L. Kastens and J. L. Ayo, Jr., *Ind. Eng. Chem.*, 42, 1626–1638 (1950).

(h) Alkyl Aryl Sulfonates

The surface-active agents produced at present in the greatest quantities and produced most cheaply are the alkyl aryl sulfonates, which have an aromatic group interposed between the alkyl and sulfonate groups:

$$CH_3(CH_2)_x \left\langle \right\rangle SO_2ONa$$

In commercial products of this type, the alkyl group often has a branched chain, as long, straight chain products are relatively insoluble. Twitchell reagents, which are used for fat splitting, are of this type:

$$CH_3(CH_2)_x CH(CH_2)_y COOH$$

 SO_2OH
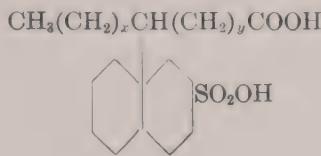
Only occasionally is the alkyl group in these materials derived from fatty acids. The usual raw material is a selected "keryl" petroleum fraction in the kerosene range, which is chlorinated to form a mixture of alkyl chlorides. These are condensed with benzene (or toluene, etc.) in a Friedel-Crafts reaction, and the alkylated aromatic is sulfonated and neutralized.

The more popular derivatives of benzene or its homologs are represented by the older proprietary Nacconol and Santomerse products, as well as a host of more recent ones, e.g., Oronite, Kreelon, Ultrawet, etc. At present, a number of packaged household detergents, e.g., Swerl, are known to consist wholly of this type of surface-active agent; it has been used on occasion by manufacturers who depend primarily on other types.

Triton 720, although made by an entirely different procedure, is similar to the above, except that it has an ether linkage between the benzene ring and the sulfonate group.

Propylated and butylated naphthalene, diphenyl, and phenylphenol sulfonates (Nekals A and B, Aresket, Areskap, etc.) are produced in some quantity as wetting agents and penetrants.

6. CATIONIC COMPOUNDS

The commercially important cationic surface-active agents are built around the basic structure:

$$\left[\begin{array}{c} a \\ | \\ R-N-b \\ | \\ c \end{array} \right]^{+} \quad X^{-}$$
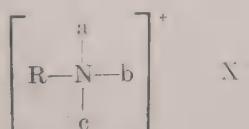
which is in many cases derived from a fatty amine prepared by catalytic hydrogenation of the corresponding nitrile (page 765). The radical, R, in the above formula is usually an alkyl radical, although there may be a more complex chain or an ester, amide, or ether linkage with the basic nitrogen atom. The anion, X, is usually a halogen, although there are other groups that may be used, such as the acetate, sulfate, or sulfonate. The groups designated as a, b, and c may consist of unsubstituted hydrogen atoms, as in the alkyl ammonium hydrochlorides:

$$R.NH_2HCl$$

they may be methyl groups or other organic radicals of low molecular weight, as in the alkyl trimethylammonium chlorides, *e.g.*, Arquads, Retarder LA:

$$\left[\begin{array}{c} CH_3 \\ | \\ R-N-CH_3 \\ | \\ CH_3 \end{array} \right]^+ \qquad Cl^-$$
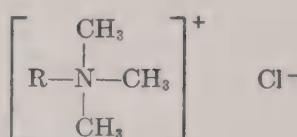
or the highly popular alkyl dimethylbenzylammonium halides, *e.g.*, Triton K-12 and K-60, Ammonyx, Octab:

$$\left[\begin{array}{c} CH_3 \qquad\quad CH{=}CH \\ | \qquad\qquad\quad / \qquad\backslash \\ R-N-CH_2-C \qquad\qquad CH \\ | \qquad\qquad\quad \backslash \qquad / \\ CH_3 \qquad\quad CH{-}CH \end{array} \right]^+ \qquad Cl^-$$
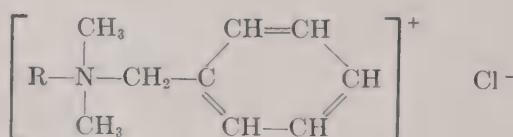
or they may form part of an aromatic ring, as in the alkyl pyridinium halides, *e.g.*, Emulsol 660B, C.P.B., Lissolamine A:

$$\left[\begin{array}{c} CH{=}CH \\ / \qquad\backslash \\ R-N \qquad\qquad CH \\ \backslash \qquad / \\ CH{-}CH \end{array} \right]^+ \qquad Br^-$$
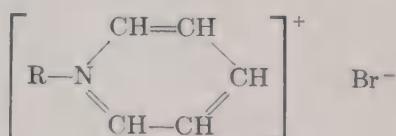
Compounds in which complete substitution of the hydrogen atoms has taken place are termed *quaternary ammonium compounds*.

An important group of surface-active agents with the latter structure consists of compounds, exemplified by Zelan:

$$\left[\begin{array}{c} CH{=}CH \\ / \qquad\backslash \\ R-CONH-CH_2-N \qquad\qquad CH \\ \backslash \qquad / \\ CH{-}CH \end{array} \right]^+ \qquad Cl^-$$
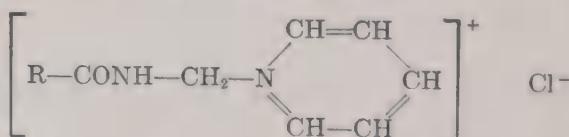
which, when applied to fabrics and then decomposed by heat, yield a wash-resistant water-repellent coating.

The cationic agents have surface-active properties which are, in general, similar must those of anionic compounds of comparable structure and

chain length. Since the long chain ion is positively charged, they are, of course, completely resistant to hard water. Their cationic nature, in addition, confers special adsorptive characteristics which are valuable in textile processing and other special applications.

One of the distinctive properties of the quaternary ammonium compounds which has promoted their use and gained for them a considerable market in spite of a relatively high cost, is their strong germicidal action. They are particularly desirable for hospital use and for washing or rinsing dairy equipment and dishes and glassware in public places where food is served, and for other applications where sanitary considerations are important.

7. Nonionic Compounds

As detergents or wetting agents, water-soluble nonionic agents have the advantage of being completely insensitive to calcium, magnesium, or other heavy metal ions, of generally being stable over a wide pH range, and of rinsing more readily from textile fibers, etc., than ionic agents. However, the most useful characteristic of these materials as a class is perhaps the ease with which their molecular structure can be varied, in gradual and controlled steps, to yield compounds ranging from those that are oil-soluble and strongly lipophilic, to others that are water-soluble and predominantly hydrophilic. The fact that the relative strengths of the lipophilic and hydrophilic properties can thus be controlled makes the nonionic surface-active materials particularly suitable emulsifying agents. As explained previously, satisfactory emulsification and the production of a stable emulsion often requires a nice balance between these two opposed properties, and it is advantageous to be able to produce virtually a "tailor-made" molecule for any specific application.

(a) Partial Esters of Polyhydric Alcohols

Partial esters of polyhydric alcohols are, with the exception of certain polyglycerol products, oil-soluble, but only very sparingly soluble in water. The best known preparations of this type are the commercial monoglycerides, which are used in large quantities as emulsifying agents in shortenings (p. 255) and in smaller amounts in many other applications.

Commercial monoglycerides as usually manufactured, are actually a mixture of mono, di-, and triglycerides (page 836), and also often contain free glycerol, as well as small amounts of soaps used as catalysts in their manufacture. Although methods are known for producing substantially pure monoesters, they are relatively difficult, hence the glycerol products on the market, as well as those based on other poly   dric alcohols, are usually mixtures. Diglycerides have relative   surface

activity (page 826). Similarly, commercial products labeled "stearate," "oleate," etc., are seldom even substantially pure.

In addition to the monoglycerides, there are also available monoester preparations based on glycols, *e.g.*, Emcol 50 series, polyglycerols, pentaerythritol and dipentaerythritol (Pentamuls), and sorbitol and its anhydrides (Spans).

(b) *Ethylene Oxide Condensation Products*

As explained previously (page 389), any compound containing a free hydroxyl group can be reacted with ethylene oxide to enhance its hydrophilic properties to whatever degree is desired. Some of the popular polyoxyethylene products are thus derived from partially esterified polyhydric alcohols, *e.g.*, Vanade, used as an emulsifying agent in bakery products, is an ethylene oxide addition product of sorbitol partial esters, and the Tweens are similarly based upon the sorbitol partial esters or Spans referred to above. Myrj, widely used as a "bread softener" is a fatty acid–ethylene oxide condensation product; Sterox is a polyoxyethylene ether.

Certain surface-active agents that have been widely used, particularly in Europe, are analogous products of fatty alcohols (*e.g.*, Leonils O and C, Emulphor O) or alkyl phenols (*e.g.*, Igepals C, F, and W, Emulphors A and ELN, Leonils FFO and WS, and Triton NE). Each of the above series of trade names also includes members which are anionic agents prepared by sulfation of the nonionic material.

8. OTHER SYNTHETIC SURFACE-ACTIVE AGENTS

A number of synthetic surface-active agents, many of which are oil-soluble rather than water-soluble, come under none of the above categories. These include additives for improving the metal adhesion of lubricating oils, such as methyl dichlorostearate,[121] additives for extreme-pressure lubricating greases, which usually contain sulfur in the sulfide form, crystallization inhibitors for lubricating oils (pour point depressants)— for which a wide variety of materials have been patented, heavy metal compounds used to prevent sludging and sludge deposition in crankcase and Diesel engine oils, long chain additives for rust-preventive oils and greases, sulfurized oils used in cutting oil preparations, metal soaps used to enhance the oil-wetting properties of paint pigments, the xanthates and pine oil derivatives used as collectors and frothing agents in ore

[121] G. L. Clark, B. H. Lincoln, and R. R. Sterrett, *Proc. Am. Petroleum Inst., III.* 16, 68–80 (1935). L. L. Davis, B. E. Sibley, and B. H. Lincoln, *ibid.*, 16, 81–103 (1935); *ner & Natural Gasoline Mfr., 14*, 523–536 (1935). B. H. Lincoln, G. D. Byrkit, a L. Steiner, *Ind. Eng. Chem., 28*, 1191–1197 (1936).

flotation, and the higher alcohols, *e.g.*, octyl alcohol, used as antifoaming agents.

9. MIXTURES OF SURFACE-ACTIVE AGENTS

Although more than one surface-active agent is sometimes used at the same time by the consumer, relatively few of the proprietary preparations on the market are mixtures. A list of these is given by Sisley.[115]

10. NATURAL FATTY SURFACE-ACTIVE AGENTS

The *phosphatides* are properly classed with surface-active agents derived from fats, although they are natural rather than manufactured products. Structurally, the phosphatides consist of glycerides in which one fatty acid radical has been replaced with phosphoric acid. In the case of lecithin, the phosphoric acid is further esterified with choline; in cephalin it is similarly esterified with cholamine. The lipophilic portion of the molecule consists of the fatty acid radicals, while the phosphoric acid–choline or phosphoric acid–cholamine complex comprises the hydrophilic group.

Most of the phosphatides of commerce are derived from soybean oil and are marketed as "soya lecithin," although there is a minor production of corn oil phosphatides. In its usual form, soya lecithin is a stiff, waxy, dark yellow or orange-brown solid containing from 30 to 35% of free soybean oil. The remainder of the product consists largely of phosphatides, although minor proportions of sterols, carbohydrates, glycosides, etc., are also present, since the mixture is separated from the crude oil by hydration, and further processing consists only of removal of the water of hydration and possibly bleaching, without fractionation of the mixture. The phosphatides in soya lecithin are said to consist of inositol phosphatides, as well as lecithin and cephalin. Commercial lecithin has a slight characteristic flavor and odor reminiscent of the parent crude oil. This flavor and odor, however, is not detectable in the concentration in which lecithin is used in food products (usually less than 0.5%). For use in the confectionery industry a special grade of soya lecithin is available, in which the soybean oil is dissolved out of the mixture with acetone (in which the phosphatides are insoluble) and replaced with an equivalent amount of cocoa butter.

The commercial lecithins are effective oil-soluble emulsifying and dispersing agents. They are edible, and probably their most important use is in food products. They are extensively used as emulsifying and anti-spattering agents for margarine, particularly in Europe; in the United States, mono- and diglycerides and their derivatives have, to some extent,

replaced lecithin for this purpose. They are very extensively used in the confectionery industry as assistants in the manufacture of chocolate products. The addition of 1% of lecithin or less to the cocoa butter–cocoa solids–sugar–water mixture used as a chocolate coating greatly reduces its viscosity, due to the dispersive effect of the lecithin upon the solid particles in the mixture. Thus with the aid of lecithin sufficiently fluid coatings may be prepared without the use of large proportions of relatively expensive cocoa butter. Lecithin also aids in the prevention of "bloom" on the surface of chocolates, through its dispersive action upon crystals forming on the surface. Lecithin has also been claimed as a desirable surface-active agent for addition to shortenings and various bakery products, but its use for these purposes, in the United States at least, is very limited.

A considerable quantity of lecithin is used in the petroleum industry, principally for addition to lubricants to inhibit gum formation. The list of other products to which the addition of this material has been recommended or patented is very long and includes various cosmetics and pharmaceutical preparations, textile-processing preparations, leather-processing compositions, soaps and other detergents, adhesives, and insecticides. It is rather difficult to assess the value of lecithin in these miscellaneous applications; however, in some its effectiveness would appear to be dubious. For detailed information on the processing and uses of lecithin, reference may be made to the recent review of Stanley[122] (see also page 625). The present consumption of lecithin in the United States is in the neighborhood of 8.5 million pounds yearly.[122]

The prolonged heat treatment of a fat or oil in contact with the atmosphere invariably results in the development of a certain amount of surface-active materials *in situ*. The reactions leading to the production of surface-active substances in heat-treated oils are diverse and complex. It can be said with certainty, however, that these substances do not consist simply of free fatty acids, but are other oxidation products, containing among other things a multiplicity of free hydroxyl groups. A well-known example of surface action deriving from such materials is that observed in blown drying oils. The effectiveness of palm oil or other tinning oils appears to depend upon surface-active substances which are produced in the oil during its use in the tinning bath.[123]   In the frying of doughnuts or similar foods, a certain content of oxidation products in the frying fat is requisite for proper browning of the fried products.

A number of other natural surface-active agents, such as the saponins

[122] J. Stanley, Chapter XVI in *Soybeans and Soybean Products*, K. S. Markley, ed., Int. Science. New York. 1950–1951.
[123] S. W. ... and K. S. Markley, *Oil & Soap*, **20**, 1–11 (1943).

and the bile acids, are found in plants or animals, where they often perform an important biological role, but none of these are, strictly speaking, of a fatty nature, and they have no great industrial importance.

However, there is a limited use of sterols as emulsifying agents in cosmetic and pharmaceutical preparations, because of their stability over a very wide pH range.

F. Applications

The industrial applications of surface-active agents are so many and diverse that no more than a bare outline of the subject can be attempted here. As pointed out by Snell[124] "whenever liquid–solid or liquid–liquid interfaces occur, surface activity is a factor," and there is scarcely any process involving the production of such interfaces where surface-active agents are not of present or potential importance.

1. DETERGENTS

Much the most important use of surface-active agents is as detergents or cleaning materials. Tremendous quantities of these materials are required, in homes, in public service institutions, and in industrial plants. Since soap is actually superior to any other class of detergents for many purposes, and is acceptable although not superior for others, and since it is much the cheapest detergent, its use far outweighs that of all other cleaning materials. However, the fact that it cannot be used except in alkaline solution and that it reacts with hard water, has caused it to be replaced to some extent by other and newer detergents in certain special applications.

There is a certain distinction to be made between the use of detergents in manufacturing plants and in other places, including the home. The principal use of detergents in places of the latter class is to clean clothes, linens, dishes, floors, etc. Detergents which are designed for such use must actually be "all-service" materials. Both the dirt and the dirty surfaces may vary widely in character, and the cleaning problems which arise will seldom be definite and clearcut. In manufacturing processes, however, a detergent is usually used to remove a specific substance, usually of an oily nature, from a specific type of surface. In such an application it is possible to select the detergent upon the basis of its ability to perform a particular job. For this reason, the newer, nonsoap detergents have heretofore achieved rather greater importance in industrial use than in the household, although in the latter field they are now gaining ground very rapidly.

[124] F. D. Snell, *Ind. Eng. Chem.*, *35*, 107–117 (1943).

2. WETTING AND DEWETTING AGENTS

Probably the largest single user of wetting agents is the textile indus-try, which employs large quantities of sulfonated oils and other materials of the nonsoap variety as textile assistants, to enable dyestuffs to be easily and evenly absorbed by the textile fibers. As "levelling agents" for dyeing surface-active agents appear to be effective because of their tend-ency to become strongly adsorbed on the textile fibers, where they delay the too-rapid adsorption of the dyes and consequent uneven coloration. Wetting agents are also used in mercerization and other chemical finish-ing treatments applied to textiles, to promote rapid and uniform action on the part of the finishing agent. Actually, surface-active agents per-form a variety of functions in textile processing other than wetting. In processing crude fibers and in desizing and deoiling operations, they act as detergents, and the sulfonated oils in many cases are used as fiber lubricants.

Recently, the treatment of fabrics for water repellence has become a highly important operation. The treating agents used are applied in the form of a surface-active solution (page 398), and eventually form a hydrophobic film. In treating a fabric for water repellence, as distin-guished from waterproofing, the material used for treatment does not form a continuous film within the fabric, but is merely deposited, in rela-tively small amount, upon the surface of the fibers, where it decreases the wettability of the fabric to such an extent that the pores are not readily penetrated by water droplets. Thus the fabric may retain its original appearance and permeability to air while achieving a considerable degree of waterproofness.

Wetting agents are often added to adhesives to overcome conditions under which an untreated adhesive will be inclined to wet one or the other of the two adhering surfaces insufficiently. Wetting agents may also be used to promote adhesion between solids and other substances which are liquid only at the time at which they are applied to the solids. Examples of solid–solidified liquid systems are dried paint films, oiled fabrics, rub-ber articles containing textile fibers or fillers, etc.

Commercial lecithin is much used as an oil-soluble wetting agent in the manufacture of chocolate confections. It serves to minimize cohesion between solid particles in the heated chocolate mass, and thus lowers its viscosity, permitting the incorporation of large proportions of sugar. It also reduces the tendency to "bloom" on chocolate surfaces through its dispersive effect on solid crystals deposited from the chocolate fat.

Among the other uses of materials active at liquid–solid interfaces are for dis wsive agents in latex suspensions, as wetting and deflocculating ints in must pics manufacture, as wetting agents in paper manufacture.

as wetting agents in the acid treatment of oil wells, and as wetting agents to prevent the adherence of gas bubbles and consequent pitting in electro-plating.

The most important class of wetting inhibitors consists of the "collectors" used in ore flotation. Water to which these substances have been added will completely wet the worthless gangue of ore concentrates, but will only incompletely wet particles of valuable mineral. Through the medium of a second surface-active agent designed to produce a froth, air bubbles become attached to the unwet surfaces of the mineral particles, carrying the latter away in a floating foam. The collectors principally used consist of xanthates and other compounds which are not derived from fatty materials, although there is a considerable use of higher fatty acid amine salts on certain ores, including potassium ores.

It is common practice to add water-soluble wetting agents to insecticide sprays, to improve the spreading and covering properties on plant surfaces, and retention on such surfaces. Soaps are used in most sprays, although other surface-active agents are required for preparations which contain lime and hence are incompatible with soaps. Wetting agents may also improve the effectiveness of insecticides, fungicides, or bactericides which kill upon contact.

Wetting agents are often incorporated in polishes and cleaners of the paste type, to enable these materials to make efficient contact with the surfaces to which they are applied. They are also of value in the manufacture of cosmetics, inasmuch as the efficiency of many of these products depends upon their wetting or adhesive action.

Lubricating oils are improved by the addition of small proportions of certain oil-soluble polar compounds. These increase the "oiliness" and the film strength of the oil, through the formation of oriented films upon the surfaces of the bearing metal. Oil-soluble wetting agents are also essential constituents of penetrating oils.

The surface-active agents which are active in paints, varnishes, and enamels, and which maintain the pigments of these in a suitably dispersed condition, consist usually of compounds produced *in situ* in the drying oil vehicle, through hydrolysis or oxidation of the drying oil. The selection of a drying oil with a high free fatty acid content for pigment grinding is in effect equivalent to the use of a wetting agent, inasmuch as the free acid forms metallic soaps with the pigments. However, there is said to be some use of added wetting agents such as alkyl amine and alkyl pyridinium derivatives in pigment grinding. In the manufacture of nitrocellulose lacquers the plasticizing agent usually serves as a wetting agent for the pigment, but with some nonpolar plasticizers the addition of other wetting agents is desirable.

3. Emulsifying Agents

A tremendous variety of industrial products are prepared and marketed in the form of emulsions. In addition, emulsions are formed in intermediate stages of the processing of many materials.

In one respect the use of emulsifying agents is essentially different from that of wetting agents. Whereas some degree of wetting will usually occur without the benefit of a wetting agent, it is impossible to produce an emulsion without an emulsifying agent. An emulsion is a fundamentally unstable system. Wetting agents may be said to merely assist the wetting process; in emulsification the emulsifying agent plays a dominant role. In some cases emulsifying agents are naturally present in the materials used to produce the emulsion. Where they are not present, however, they must be added.

There are instances where the production of an oil-in-water emulsion is merely a means of uniformly distributing a relatively small volume of the oil phase over a relatively large surface. Because of the high viscosity of oils, as compared with water, such distribution of an oil alone is difficult. Where the emulsion serves merely as an oil carrier, a permanent emulsion is not desired, as the aqueous phase must be removed after it has served its purpose in transporting the oil.

The outstanding use of an emulsion to distribute an oil is in the operation of "fat liquoring," as carried out in the leather industry. In this operation wet skins are caused to take up a controlled amount of oil by tumbling in a drum containing the emulsion. Since the pH of the water phase may be relatively low, the emulsifying agent most commonly used consists of a sulfonated oil, although soap is sometimes used.

Another example of emulsification for the sake of oil distribution is to be found in the so-called self-polishing floor waxes, which are emulsions of waxes in water, stabilized by ethanolamine soaps or other soaps. After the emulsion is applied, it breaks down through evaporation of water or ammonia, leaving the wax in the form of a thin, uniform, waterproof film. A very similar action takes place in the new water-thinned emulsion paints. In these, nonfatty materials, such as casein or soybean protein products, usually are the effective emulsifiers, although synthetic agents may also be used.

In the copolymerization of styrene and butadiene for the manufacture of synthetic rubber a surface-active agent capable of forming micelles (soap) is used to promote the reaction. A sizable proportion of the total industrial consumption of soap (125 million pounds in 1945) is accounted for by the synthetic rubber industry.[125] The Twitchell reagents used in

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[125] W. ̇ W. ̇ ̇mon, *J. Am. Oil Chem. Soc.*, *24*, 33–36 (1947).

fat splitting (page 800) are surface-active agents (alkyl aryl sulfonates).

Synthetic emulsifying agents are essential ingredients of soluble cutting oils for metal machining, of many cosmetic preparations, and of certain pharmaceutical products.

Among the popular food products there are a number of emulsions, including butter, margarine, ice cream, and mayonnaise and salad dressings. Margarine is relatively lacking in the phosphatide and protein compounds which stabilize butter, hence is frequently fortified with emulsifying agents, to prevent "leaking" while the product is in storage, and spattering during cooking operations. Emulsifying agents are commonly added to salad dressings. The addition of mono- and diglycerides to ice cream is also claimed to be beneficial, inhibiting the formation of large ice crystals and promoting the incorporation of air in the product.

The most important use of synthetic emulsifying agents in the food industry is in the addition of mono- and diglycerides to vegetable shortenings, to produce a special fat for cake baking. The presence of these materials in the shortening enhances the degree to which it may be dispersed in the cake dough, produces a dough of superior mechanical strength, and hence permits the use of high proportions of sugar and milk.

As mentioned (page 338), a surface-active agent that produces the formation of one type of emulsion may, when judiciously used, break an emulsion of the contrary type. The most important use of such agents as emulsion breakers is in the processing of natural crude oil emulsions in the petroleum industry.

4. Foaming and Antifoaming Agents

Much the most important use of foaming agents, as explained previously, is in ore flotation. There is also a considerable use of such agents in the production of foams for firefighting, and a few minor industrial processes, for example, in the manufacture of sponge rubber.

From an industrial standpoint, the suppression of foams is more important than foam production. Although a great variety of antifoaming agents have been patented and used, the most common are straight chain alcohols of medium molecular weight, such as octyl alcohol.

5. Dispersing and Deflocculating Agents

Surface-active agents are widely used to assist in the dispersion and deflocculation of finely divided solid particles in such industrial suspensions as paints, printing and writing inks, textile dyes, and drilling muds. They may also serve to prevent the undesirable deposition of s   ls from

a liquid as the latter undergoes use, as in the case of the antisludging and antigumming compounds added to crankcase oils.

6. Crystallization Modifiers and Inhibitors

Surface-active agents are used to inhibit crystal formation, as in the pour point depressants used in lubricating oils, and to modify habits of crystal growth, *e.g.*, in electroplating.

PAINTS, VARNISHES, AND RELATED PRODUCTS[1]

A. Introduction

Paints, varnishes, and other decorative and protective coatings, including printing inks, comprise one of the three major fields of oil and fat utilization. In 1947, the factory consumption of oils in paints and similar products in the United States amounted to 612,324 thousand pounds (Table 91B, page 425). While this amount of oil was considerably less than that consumed in soap in the same year (2,354,000 thousand pounds), or in the manufacture of shortening, margarine, and other edible products (2,915,000 thousand pounds), it exceeds the oil used in any other single class of products (see Table 29B, page 118).

The drying oils owe their value as materials for protective coatings to their ability to polymerize or "dry" after they have been applied, to form tough, adherent, impervious, and abrasion-resistant films. Their film-forming properties are closely related to their degree of unsaturation, since it is through the unsaturated centers or double bonds that polymerization takes place. With the exceptions to be noted later, the oils used in paints, varnishes, and similar products are relatively high in iodine value. In any given product, there is an optimum degree of reactiveness in the oil; the speed with which the oil dries must be balanced against such factors as elasticity and durability in the paint film. In general, however, unsaturation may be said to be at a premium in paint and varnish oils, and the oils which are in the greatest demand are those in which oxidation and polymerization take place most readily.

Until quite recently, the oils consumed in paints, varnishes, etc., consisted entirely or almost entirely of oils with pronounced drying properties, belonging to the linolenic and conjugated acid groups. Lately, however, synthetic resins of strong polymerizing properties have become available for use in varnishes and enamels in place of natural resins. With these materials it has become possible to make a considerable use

[1] GENERAL REFERENCES: H. K. Dean, *Utilization of Fats*, Chemical Pub. Co., New York, 1938. C. Ellis, *Printing Inks*, Reinhold, New York, 1940. W. von Fischer, ed.. *Paint and Varnish Technology*, Reinhold. New York, 1948. N. Heaton. *Outlines of Paint Technology*, 2nd ed.. Lippincott. London. 1940. J. J. Mattiello, ed.. *tective and Decorative Coatings*. Vol. I. Wiley. New York. 1941; Vol. III. 194 ̊ ol. IV, 1944. Oil and Colour Chemists' Assoc., *Varnish Making*, Chemical . N . . York, 1940.

of oils with poor drying and, in some cases, even nondrying properties. In these latter products, the function of the oil is more that of a plasticizer than an active drying ingredient. Also, significant quantities of a strongly drying oil are now made artificially, by the dehydration process, from castor oil, which in its natural state is completely nondrying. Additional processes have been developed to varying degrees of perfection for conferring drying ability upon other oils which are naturally deficient in this property. None of these latter processes is of great commercial importance at the present time, but together they constitute a potential means of supplementing present sources of paint and varnish oils from materials which have heretofore been devoted to other uses.

TABLE 91A

FACTORY PRODUCTION (THOUSANDS OF POUNDS) OF PAINTS, VARNISHES, AND SIMILAR
PRODUCTS IN UNITED STATES IN 1947[a]

White lead in oil	73,325	Metallic paints (aluminum, etc.).	6,573
Other paste products	4,576[b]	Other paints	19,601
Semipastes, oil and alkyd vehicles	6,908	Spirit varnishes (except shellac).	1,682
		Shellac	5,328
Read-mixed paints, oil and alkyd	105,120	Natural resin varnishes	12,521
Mill whites	3,915	Synthetic resin varnishes	51,813
Bituminous paints (except roof coatings)	18,068	Drying japans and dryers	3,990
		Baking japans	2,305
Undercoatings and primers	24,872	Enamels	90,354
Resin emulsion paints	17,187	Noncellulose lacquers	5,696
Barn and roof paints (except bituminous)	5,165	Nitrocellulose lacquers	41,793
Marine paints	10,242	Other cellulose lacquers	3,542

[a] U. S. Bureau of the Census, *Census of Manufactures, 1947.*
[b] Thousands of gallons.

Modern requirements in protective coatings are extremely diverse and in many cases exacting. They go far beyond the mere necessity of protecting the finished surface from the weather or from ordinary wear or abrasion. Some coatings, for example, those employed as electrical insulation, must possess extreme resistance to high temperatures, or to penetration by moisture. Others, such as marine varnishes, and enamels for the interior of tin cans, must withstand prolonged contact with water or aqueous solutions. The exigencies of modern, assembly line methods of manufacture produce many particular requirements, and have created an especial demand for quick-drying finishes. Since tung and other conjugated acid oils are particularly suitable for the manufacture of such products consumption of these oils has increased greatly in recent s.   distribution of illustrated journals and advertising

matter and the development of high-speed printing processes have greatly elaborated the requirements of users of printing inks.

The exacting requirements of modern industry have to a large extent removed the manufacture of paints and varnishes from the category of an art to that of a science. In most plants the manufacturing processes are now carried out under careful laboratory control, and are freely modified or revised, whenever revision is indicated, in accordance with known scientific principles. As a result, the industry has been able to offer a succession of constantly improved products through a period marked by severe fluctuations in the availability of many important raw materials.

An important development in the modern paint and varnish industry has been the introduction of synthetic resins as replacements for natural resins in the manufacture of varnishes and enamels. By use of the synthetic resins it has been possible to produce a variety of coatings which in many cases have important points of superiority over any of those compounded from natural resins. The synthetic varnishes and enamels are particularly distinguished by their hardness and durability and their high degree of resistance to the action of water, alkalies, and other chemical agents.

The widespread use of synthetic resins has increased the relative demand for conjugated acid oils, inasmuch as some of these resins, particularly those of the phenol-formaldehyde variety, are most successfully compounded with this type of oil.

B. Mechanism of Polymerization and Drying

When a paint, varnish, or other oil or oleoresinous coating material is applied to a surface, the applied film changes gradually from a liquid to a firm, tough, and durable solid. The phenomenon bears a superficial resemblance to the change occurring in aqueous systems with the evaporation of water, and hence has been termed "drying." Actually, of course, the term is a misnomer. Although some evaporation of a volatile solvent usually takes place, the essential process in the transformation of the film is one of polymerization.

Ordinary air drying always involves some amount of oxidation. Early in the history of protective coatings it was discovered, however, that polymerization could be hastened, and certain products improved by the judicious application of heat. Modern industrial finishes are very commonly "dried" by baking the coated articles at an elevated temperature. It is also a common practice, and a much older one, to partially polymerize or "body" the oil or oleoresinous vehicle by heat befo it is applied, thereafter adding a volatile "thinner" to reduce th osi and promote ease of application. This technique not ce

faster drying material, but also one dissimilar in other important respects to one that dries through oxidation alone.

The drying of oils has been observed through many centuries, and the mechanism of drying has long been under investigation by chemists and physicists. These investigations have by no means been fruitless; they have, on the contrary, revealed much information of both practical and theoretical value. A complete and generally accepted theory of oil bodying and drying has yet to be advanced, however, and many fundamental considerations are still subjects of controversy.

Recent reviews on the subject of oil polymerization, which include more or less comprehensive but divergent theories of the process are those of Von Mikusch and Priest,[2] Rudd,[3] Hollis,[4] Petit,[5] Sunderland,[6] Bradley,[7] Bradley and Tess,[8] Powers,[9] and Long.[9a]

1. EXTENT OF MOLECULAR AGGREGATION

Dried paint films possess the elasticity, cohesiveness, and homogeneity which are characteristic of the typical gel structure. They are infusible and to a considerable extent insoluble in ether, acetone, and other oil solvents. Obviously, they represent a state of molecular aggregation very different from that in the undried oil. Consequently, a great many of the older investigations[10-15] have been concerned with attempts to determine the average molecular weights of the thickened or gelled oils and their soluble and insoluble fractions in different solvents. Unfortunately, such determinations are beset with considerable difficulty. It is impossible to examine the portions of oil which have completely gelled, because of their lack of solubility, and results on the thickened oils cannot be accepted with complete confidence, due to certain limitations which are inherent in the methods of molecular weight determination. Regardless of the limitations of the methods, however, it appears obvious that no advanced degree of polymerization or association occurs up to the point of actual gelation. No fractions have been isolated from the thickened products in a state of aggregation exceeding that of tetramers of

[2] J. P. von Mikusch and G. W. Priest, *Oil & Soap*, *18*, 50–59 (1941).
[3] H. W. Rudd, *Paint Manuf.*, *13*, 95–103 (1943).
[4] C. E. Hollis, *J. Oil Colour Chem. Assoc.*, *27*, 67–91 (1944).
[5] J. Petit, *Peintures, pigments, vernis*, *20*, 2–11 (1944).
[6] E. Sunderland, *J. Oil Colour Chem. Assoc.*, *28*, 137–167 (1945).
[7] T. F. Bradley, *J. Oil Colour Chem. Assoc.*, *30*, 225–244 (1947).
[8] T. F. Bradley and R. W. Tess, *Ind. Eng. Chem.*, *41*, 310–319 (1949).
[9] P. O. Powers, *Ind. Eng. Chem.*, *41*, 304–309 (1949).
[9a] J. S. Long, *J. Oil Colour Chem. Assoc.*, *32*, 377–445 (1949).
[10] B. P. Caldwell and J. Mattiello, *Ind. Eng. Chem.*, *24*, 158–162 (1932).
[11] E. Elöd and U. Mach, *Kolloid-Z.*, *75*, 338–348 (1936).
[12] J. W. Long and W. J. Arner, *Ind. Eng. Chem.*, *18*, 1252–1253 (1926).
[13] and J. G. Smull, *Ind. Eng. Chem.*, *17*, 138–141 (1925).
[14] and G. Wentz, *Ind. Eng. Chem.*, *17*, 905–908 (1925).
G. Wentz, *Ind. Eng. Chem.*, *18*, 1245–1248 (1926).

the original oil, and in most cases the average molecular weight of the whole oil appears to approximate that of a trimer.

The fatty acids recovered from polymerized oils by hydrolysis of the latter have in all cases consisted of monomeric and dimeric compounds.[16]

The probable structure of drying oil gels was likened by Kienle[17] to that of a "brush heap" or "log jam," in which a relatively small proportion of a highly developed polymer is intertwined and interlocked in such a manner as to hold enmeshed a relatively large proportion of liquid oil in a low state of polymerization. It has been noted by Long and co-workers,[18] that well-dried films may contain 70% or more of acetone-soluble oil.

As pointed out by Bradley and Johnston,[19] the presence of liquid fractions in drying oil gels is not necessarily due to the polymerization being incomplete, but may rather be attributed to the production of heat-altered esters which have lost their ability to intercombine, due to intra-molecular cyclization, or other causes. However, there is ample evidence that fresh gels are ordinarily in a state of polymerization considerably short of their potentialities in this respect. There is apparently a progressive polymerization in paint films over a period of months or even years.[18] Steger and van Loon[20] reported that gelation occurred in heat-treated tung and linseed oils when only 50% of their unsaturated acids had dimerized. Bradley and Richardson[21] found 30% of the conjugated fatty acids of tung oil to be intact at the point of gelation.

The "log jam" concept of a tangle of molecules of moderate size has been somewhat modified by late work, both of an experimental and theoretical nature. It is now generally assumed, as first suggested by Carothers,[22] that at the point of gelation the continuity of linked molecules runs virtually throughout the material. Flory[23] has shown statistically that cross linking to form an extensive three-dimensional network may occur while most of the material is still in quite a low average state of aggregation (page 906). In the bodying of oils even to high viscosities, most of the polymerization that occurs is undoubtedly productive only of dimers.

2. MECHANISM OF DIMER FORMATION

The mechanism by which dimeric molecules of drying oils are formed has been a matter of much speculation. Interests in the mechanism ex-

[16] J. Marcusson, Z. angew. Chem., 39, 476–479 (1926).
[17] R. H. Kienle. J. Soc. Chem. Ind., 55, 229–237T (1936).
[18] J. S. Long, A. E. Rheineck, and G. L. Ball, Jr., Ind. Eng. Chem., 25, 1086–1091 (1933). J. S. Long, E. K. Zimmermann, and S. C. Nevins, Ind. Eng. Chem. 20, 806–809 (1928).
[19] T. F. Bradley and W. B. Johnston, Ind. Eng. Chem., 32, 802–809).
[20] A. Steger and J. van Loon, Fettchem. Umschau, 43, 17–21 (19
[21] T. F. Bradley and D. Richardson, Ind. Eng. Chem., 32, 9f
[22] W. H. Carothers, Trans. Faraday Soc., 32, 39–5
[23] P. J. Flory, J. Am. Chem. Soc., 63, 3083–309f

tends beyond the initial stage of polymerization, inasmuch as the reaction which produces the dimer may logically extend to the formation of the larger aggregates which are assumed to exist in the gel or solidified paint film.

It is now generally believed that the fatty acid radicals in polymerized oils are joined predominantly by carbon-to-carbon bonds established through a Diels-Alder reaction,[24] as first proposed by Kappelmeier:[25]

$$
\begin{array}{ccc}
\underset{\displaystyle X-\overset{\displaystyle\|}{C}}{}\;\overset{\displaystyle C-C}{}\;\underset{\displaystyle C-Y}{} & \longrightarrow & \underset{\displaystyle X-C}{}\;\overset{\displaystyle C=C}{}\;\underset{\displaystyle C-Y}{} \\
X'-C=C-Y' & & X'-C\text{——}C-Y'
\end{array}
$$
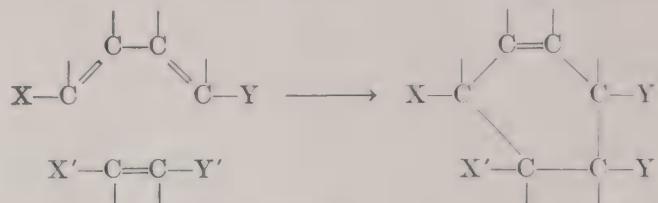
It will be noted that the union of two fatty acid radicals by a Diels-Alder reaction requires the presence of conjugated double bonds in one of the fatty acids. Thus, in the case of nonconjugated oils, it is necessary to postulate a preliminary isomerization to yield double bonds in a conjugated position. That conjugated acids are formed during the heat bodying of ordinary oils was first deduced by Scheiber[26] from the observation that the refractive index of linseed and similar oils increases during this operation, whereas that of tung oil decreases. Positive evidence of isomerization to produce conjugated forms has since been provided by a number of investigators through examination of the ultraviolet absorption spectra of the oils. In the air drying of oil films it has been shown[27] that the amount of conjugated material reaches a maximum at about the time that the film sets, and then decreases during the subsequent curing stage.

In the above reaction it is evident that the preliminary shift of double bonds to conjugated positions occurs less readily than subsequent coupling with the nonconjugated chain, and consequently that it is the rate-controlling step. Catalysts which promote the polymerization process apparently function by accelerating isomerization.[8,28] From the relatively high densities and high refractive indices of the monoester dimers it has been postulated[19,29,30] that triethenoid esters, unlike diethenoid esters, are capable of forming polycyclic structures.

It was once generally believed that in the air drying of oil films and

[24] O. Diels and K. Alder, *Ann.*, *460*, 98–122 (1928).

[25] C. P. A. Kappelmeier, *Farben-Ztg.*, *38*, 1018–1020, 1077–1079 (1933).

[26] J. Scheiber, *Farbe u. Lack*, *1929*, 585–587.

[27] M. J. Hendrickson, R. P. Cox, and J. C. Konen, *J. Am. Oil Chem. Soc.*, *25*, 73–77 (1948).

[28] R. L. Terrill, *Oil & Soap*, *23*, 339–344 (1946); also in *Paint and Varnish Technology*, W. von Fischer, ed., Reinhold, New York, 1948.

[29] W. Bradley and W. B. Johnston, *Ind. Eng. Chem.*, *33*, 86–89 (1941).

[30] J. C. Cowan, J. P. Kass, and J. E. Jackson, *Ind. Eng. Chem.*, *34*,

in other polymerizations accompanied by oxidation, if not in heat bodying, the fatty acid chains became linked by permanent carbon-oxygen-carbon linkages. However, the preponderance of opinion now appears to be that this type of polymerization, too, proceeds through the establishment of direct linkages between carbon atoms. The different characteristics of air-blown or air-dried oils are attributed to the occurrence of side reactions, rather than to any fundamental difference in the mechanisms of polymerization *per se*. That polymerization occurs much more readily in the presence of oxygen is ascribed to the activating influence of peroxides or hydroperoxides.

3. Miscellaneous Reactions

In the monoesters of polyunsaturated fatty acids polymerization apparently may proceed as far as the trimer stage.[19,29,30] The following typical scheme is proposed:

Monomer

$$
\begin{array}{c}
\text{CH}-\text{CH} \\
X-\text{CH} \qquad \text{CH}-Y
\end{array}
$$

↓

Dimer

$$
\begin{array}{c}
\text{CH}=\text{CH} \\
X-\text{CH} \qquad \text{CH}-Y \\
\text{CH}-\text{CH} \\
X' \qquad \text{CH} \\
\text{CH}-Y'
\end{array}
$$

↓

Trimer

$$
\begin{array}{c}
\text{CH}=\text{CH} \\
X-\text{CH} \qquad \text{CH}-Y \\
\text{CH}-\text{CH} \\
X' \\
X'' \\
\text{CH}-\text{CH} \\
\text{CH} \qquad \text{CH}-Y' \\
\text{CH}-\text{CH} \\
Y''
\end{array}
$$
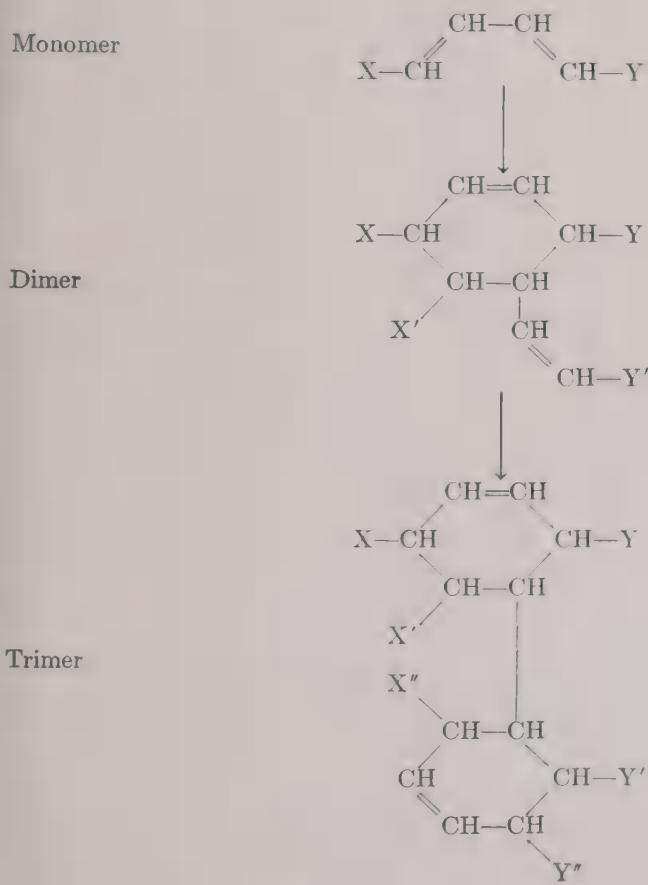
Presumably, a similar mechanism may be operative in drying oi'.

While it is difficult to interpret the experimental data

the loss of reactive groups, because of some splitting of fatty acid chains and also the low iodine absorption of conjugated compounds; nevertheless, it appears that this loss is greater than can be accounted for by the establishment of intermolecular linkages alone. Hence it is probable that extensive intramolecular cyclization occurs, within monomers as well as within larger aggregates.[31-34] It has been pointed out that such intramolecular reaction may increase the hardness and rigidity of drying oil gels, even though it does not contribute to molecular growth.[8] A suggestion has been made[32] that the Diels-Alder reaction occurs largely between fatty acid chains in the same glyceride molecule and that polymerization is a result of interchange between this intrapolymer and another glyceride.

The polymerization of drying oils is not simply an addition process; it involves condensations and other reactions productive of low moleculer weight compounds, as is shown by the fact that carbon dioxide, volatile acids, and water vapor are evolved, both in the bodying of oils under vacuum or nitrogen,[35] and in the drying of paint films.[18]

That the drying of paint films is inhibited by moisture and is much retarded by a humid atmosphere was demonstrated by Schmutz and Palmer[36] and by Long, Rheineck, and Ball.[18]

Peroxides or hydroperoxides develop rapidly during the air drying of a paint or varnish film, but of course do not appear in the course of heat bodying, oven baking of films, or other high-temperature operations. Drying and polymerization are inhibited by the presence of phosphatides[15] and other substances[37-39] which are effective as antioxidants in edible vegetable oils. They are accelerated by metallic oxides, by sulfur and selenium and their oxides[40-42] by heat, and by light.[36,43]

The heat bodying of linseed oil and various synthetic triglycerides in the presence of oxygen was studied in detail by Long and Chataway[44] and Long and McCarter.[45] At 160°C. the rate of oxygen uptake was observed to be a straight-line function of the degree of oxidation, up to the point of gelation. The gelation point, in terms of oxygen absorbed, varied

[31] T. F. Bradley and H. F. Pfann. *Ind. Eng. Chem.*, *32*, 694–697 (1940).
[32] H. E. Adams and P. O. Powers, *Ind. Eng. Chem.*, *36*, 1124–1127 (1944).
[33] H. E. Adams and P. O. Powers, *J. Applied Phys.*, *17*, 325–337 (1946).
[34] T. F. Bradley and D. Richardson, *Ind. Eng. Chem.*, *32*, 963–969 (1940).
[35] J. S. Long, C. A. Knauss, and J. G. Smull, *Ind. Eng. Chem.*, *19*, 62–65 (1927).
[36] F. C. Schmutz and F. C. Palmer, *Ind. Eng. Chem.*, *22*, 84–87 (1930).
[37] J. Scheiber, *Angew. Chem.*, *46*, 643–647 (1933).
[38] A. M. Wagner and J. C. Brier, *Ind. Eng. Chem.*, *23*, 40–49 (1931).
[39] A. M. Wagner and J. C. Brier, *Ind. Eng. Chem.*, *23*, 662–666 (1931).
[40] H. I. Waterman and C. van Vlodrop, *J. Soc. Chem. Ind.*, *55*, 333–334T (1936).
[41] H. I. Waterman, C. van Vlodrop, and F. Althuisius, *J. Soc. Chem. Ind.*, *57*, 87–89T (1938).
[42] I   wever, sulfur and selenium inhibit the gelation of tung oil.
[43]   Waele. *J. Soc. Chem. Ind.*, *39*, 48–50T (1920).
[44]   and H. D. Chataway, *Ind. Eng. Chem.*, *23*, 53–57 (1931).
[45]   W. McCarter, *Ind. Eng. Chem.*, *23*, 786–791 (1931).

considerably with different oils, from approximately 5% (by weight) in the case of alpha-elaeostearin to 15% in the case of triolein. Raw linseed oil gelled after taking up approximately 10% of oxygen, but heat-bodied oil gelled with the absorption of less than 3%. From 50 to 85% of the oxygen absorbed up to the point of gelation remained in the oil in a combined form. The remainder formed volatile products of various kinds with 3.5–5% of the carbon and hydrogen of the oil. In the case of linseed oil and also of triolein and trilinolenin, the amount of oxygen absorbed up to the point of gelation corresponded closely to that required to form one peroxide group per each molecule of unsaturated fatty acid.

The acidity of drying oils, as measured by the acid number, rises moderately in heat bodying, and quite markedly in the air drying of paint and varnish films. In the latter case, however, it is apparent that the acidic substances are largely degradation products of low molecular weight, rather than free fatty acids resulting from hydrolysis of the glycerides.[46]

"Frosting," or drying with the production of a wrinkled, folded surface is characteristic of films of conjugated acid oils. This phenomenon is due to volume changes in the oil during the process of drying; their cause is obscure. The tendency of films to frost is much enhanced by exposure to oven gases during baking and has been attributed[47] to the presence of traces of nitric oxide in the air. Eibner and Rossmann[48] reported a microscopic examination of drying tung oil films. They observed a shrinkage in volume, with the formation of small cracks, near the beginning of the drying period. Later an expansion occurred, with the production of folds at right angles to the cracks. Frosting of tung oil films is prevented by previous heat treatment of the oil. The action of the dryer is important in preventing or deliberately inducing frosting or wrinkling; the phenomenon is favored by a dryer such as cobalt, which produces pronounced "top drying," and is inhibited by a dryer which gives good "through drying."

Recently, Dannenberg and co-workers[48a] have recommended that the burners of baking ovens be so adjusted as to avoid the formation of smoke or soot, to control gas-checking. Their investigations indicated that the initial breaks in the oil film proceeded radially outward from centers where very small dust particles were lodged. Subsequent oozing of liquid oil into the cracks was observed to produce the typical check pattern.

Lately a considerable demand has arisen for wrinkle finishes, and alkyd enamels, etc., have been developed which produce a variety of novel

[46] V. J. Frilette, *Ind. Eng. Chem.*, *38*, 493–496 (1946).
[47] J. Hyman and T. Greenfield, *Ind. Eng. Chem.*, *28*, 238–241 (1936).
[48] A. Eibner and E. Rossmann, *Chem. Umschau Fette, Öle, Wachse*, *35*, 281–290 (1928).
[48a] H. Dannenberg, J. K. Wagers, and T. F. Bradley, *Ind. Er...* 1599 (1950).

effects through wrinkling. In general, a wrinkle finish is produced by applying a very thick film, which is subsequently subjected to a maximum degree of top drying. The subject of wrinkling and wrinkle finishes is discussed in detail in a recent publication of Moore.[49]

4. Concept of Functionality

Certain aspects of the phenomenon of oil drying have been greatly clarified by the concept of functionality in polymerization, as developed by Carothers[50,51] and Kienle and co-workers,[52-57] through their researches on synthetic resins, and applied specifically to drying oils by Bradley.[58,59]

According to the theory developed on the basis of this concept, the reactions occurring in polymerization are not to be regarded as necessarily different from those occurring between ordinary organic compounds. The distinguishing feature of polymerization is rather the peculiar multiplicity of these reactions.

In the molecules of the polymerizable substance, the groups which are reactive or capable of uniting to form polymers are termed "functional." Compounds containing one such group are "monofunctional"; those which have two functional groups are termed "bifunctional," etc.

For a compound to be capable of attaining a high degree of polymerization, it must be at least bifunctional. Two monofunctional molecules are incapable of further reaction after they have united to form a dimer, since all of the functional groups will have disappeared in bringing about their union. In the case of bifunctional compounds, the dimer will retain the same degree of functionality as the unpolymerized compound. One functional group from each molecule will disappear in the reaction, but the remaining two groups will remain free, to give the dimer resulting from their union a functionality of two. In each succeeding reaction a new functional group will be added to the polymer for each group that disappears, so that the polymer will continue to be bifunctional, regardless of how far polymerization is carried, unless ring closure occurs to reduce the functionality to zero. Bifunctional compounds are capable of continued linear growth, but cannot assume the three-dimensional, interlocked

[49] H. R. Moore, in *Protective and Decorative Coatings*, Vol. III, J. J. Mattiello, ed., Wiley, New York, 1943, pp. 250–266.
[50] W. H. Carothers, *J. Am. Chem. Soc.*, 51, 2548–2559 (1929).
[51] W. H. Carothers and J. A. Arvin, *J. Am. Chem. Soc.*, 51, 2560–2570 (1929).
[52] R. H. Kienle, *Ind. Eng. Chem.*, 22, 590–594 (1930).
[53] R. H. Kienle, *Ind. Eng. Chem.*, 23, 1260–1261 (1931).
[54] R. H. Kienle and P. F. Schlingman, *Ind. Eng. Chem.*, 25, 971–975 (1933).
[55] R. H. Kienle and C. S. Ferguson, *Ind. Eng. Chem.*, 21, 349–352 (1929).
[56] R. H. Kienle and A. G. Hovey, *J. Am. Chem. Soc.*, 51, 509–519 (1929).
[57] R. W. Kienle and A. G. Hovey, *J. Am. Chem. Soc.*, 52, 3636–3645 (1930).
    ley, *Ind. Eng. Chem.*, 29, 440–445 (1937).
        Ind. Eng. Chem., 30, 689–696 (1938).

structure of solid polymers. Linear polymers are, in general, liquid, fusible, and soluble in ordinary solvents.

If the compound in question has a functionality of three or more, a highly significant situation arises. Then there will be a progressive increase in the functionality of the polymer, as polymerization proceeds. Thus a trifunctional compound will possess a functionality of four at the dimeric stage, five at the trimeric stage, six at the tetrameric stage, etc. In other words, at each successively advanced degree of polymerization the polymer becomes more reactive and more capable of further molecular growth in all directions. In such compounds, polymerization rapidly results in three-dimensional cross bridging between adjacent molecular chains to form a rigid, lattice-like structure of infinitely large molecular weight. Polymers of this structure are solid, infusible, and insoluble in ordinary organic liquids.

Upon the basis of the functionality of the reacting compounds, polymerization reactions are subject to mathematical treatment leading to prediction of the degree of polymerization at which the three-dimensional structure will appear. Such treatments have been given by Carothers,[22] Kienle,[17] Flory,[23,60] and Stockmayer.[61]

Wheeler[62] has given the following values for the functionality of the double bond systems of different drying oil fatty acids:

Oleic	Greater than 0, less than 1
Normal linoleic	ca. 1
Conjugated dienoic	ca. 1
Normal linolenic	Greater than 1, less than 2
Conjugated trienoic	Greater than 1, less than 2

The functionality indicated for the isolated double bond of oleic acid has been assigned from the circumstance that triolein (glycerol ester) does not gel, although dimeric compounds have been isolated from oxidized pure methyl oleate. Since a compound with a single double bond is capable of uniting with a polyunsaturated compound by the Diels-Alder action (page 414), the functionality of oleic acid may be expected to be greater in the presence of more unsaturated acids than in a pure oleate material. A definite functionality for oleic acid in natural oils is indicated by the oil bodying studies of Anderson and Porter.[62a] That the functionality of the two dienoic acids is close to one is indicated by the fact that their glycol esters do not gel, whereas their glycerol esters form

[60] P. J. Flory, *J. Am. Chem. Soc., 58*, 1877–1885 (1936); *63*, 3083–3100 (1941); *69*, 30–35 (1947).

[61] W. H. Stockmayer, *J. Chem. Phys., 11*, 45–55 (1943).

[62] D. H. Wheeler, *Ind. Eng. Chem., 41*, 252–258 (1949).

[62a] L. V. Anderson and J. V. Porter, *Ind. Eng. Chem., 41*, 741–74᷄

hard films. The above functionality for the two trienoic acids is based on the failure of the monoesters to gel and the ability of the glycol esters to yield hard films.

From a practical standpoint, an important result of the functionality concept is a new technique for improving the drying properties of oils, *viz.*, by separating the fatty acids and re-esterifying them with a polyhydric alcohol containing more hydroxyl groups than glycerol. This technique is now actually employed quite extensively on a commercial scale, with pentaerythritol or sorbitol being used as the polyhydric alcohol. It is particularly applicable to the manufacture of alkyd resin products, which require operations of esterification or interesterification, regardless of the raw materials employed.

5. RATES OF POLYMERIZATION

Since the formation of a conjugated double bond system is prerequisite to the Diels-Adler coupling described above, it is not surprising that conjugated acid oils, which contain such a system naturally, will polymerize much more rapidly than nonconjugated oils, in which it must be induced by oxidation or heat treatment. The relative reaction rates of conjugated and nonconjugated oils, in the process of heat bodying, are shown in Figures 159 and 160.

The relative polymerization rates of normal nonconjugated fatty acids and their esters, either in heat bodying or air drying, appear to be approximately the same as their rates of oxidation (page 56); linolenic acid, for example, is reported to dimerize twice as rapidly as linoleic acid.[63] However, certain anomalies arise in highly modified or synthetic oils, *i.e.*, dehydrated castor oil or catalytically isomerized oils, which contain *trans*-acids and other fatty acids not found in natural oils. Whereas *cis*- and *trans*-isomers oxidize at quite different rates (page 55), it has been observed[30] that they polymerize with equal readiness under the influence of heat. This has the effect of vitiating the normal correlation between the rates of heat bodying and air drying, and causing oils which body readily to dry with relative slowness.[30,64]

In addition to geometric isomerism, a factor which may influence the polymerizing properties of synthetic oils is the occurrence of double bonds at abnormal positions along the fatty acid chain. That the reactivity of double bonds with respect to polymerization is highly dependent upon their distance from the end of the chain was clearly shown by the work

[63] I. M. Bernstein, *J. Phys. & Colloid Chem.*, 52, 613–661 (1948).
[64] Spitzer, R. F. Ruthruff, and W. T. Walton, *Am. Paint J.*, 26, No. 12, 68–

of Morrell and co-workers[65-68] on elaeostearic glycerides. When the alpha form of this acid is reacted with maleic anhydride, an addition product or "adduct" is formed which blocks the two double bonds farthest removed from the carboxyl group, leaving only the near linkage reactive. Similarly in the adduct formed from the beta form of the acid, the two near linkages are blocked, leaving only the far double bond reactive:

$$
\begin{array}{c}
\text{CH=CH} \\
\text{CH}_3(\text{CH}_2)_3\text{CH} \quad\quad \text{CH}.\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOR} \\
\text{CH---CH} \\
\text{OC} \quad \text{CO} \\
\text{O}
\end{array}
$$

Alpha-elaeosteric acid–maleic anhydride compound

$$
\begin{array}{c}
\text{CH=CH} \\
\text{CH}_3(\text{CH}_2)_3\text{CH}:\text{CH}.\text{CH} \quad\quad \text{CH}(\text{CH}_2)_7\text{COOR} \\
\text{CH---CH} \\
\text{OC} \quad \text{CO} \\
\text{O}
\end{array}
$$
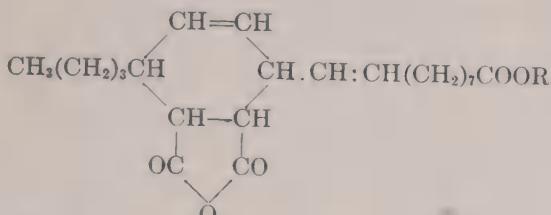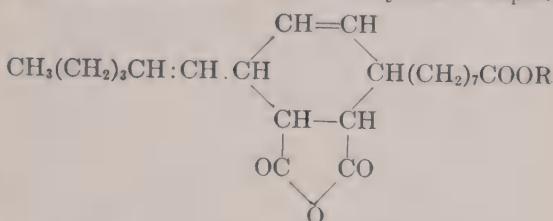
Beta-elaeosteric acid–maleic anhydride compound

By working with the addition products rather than the simple glycerides, it is thus possible to study at will the reactions of either the near or the far bond. The experimental data have revealed that the three double bonds are by no means equivalent in reactivity. The middle (11:12) linkage is virtually inert toward atmospheric oxidation; consequently, it is considered that the first stage of oxygen addition involves the formation of peroxides at the other two bonds. Peroxides are formed at the near (9:10) bond with relative slowness and are inclined to isomerize to a hydroxy-ketone group:

$$
-\text{CH=CH}- \rightarrow \begin{array}{c}-\text{CH---CH}-\\ \text{O}-\text{O}\end{array} \rightarrow \begin{array}{c}-\text{CH=C}-\\ \text{HO} \quad \text{OH}\end{array} \rightarrow \begin{array}{c}-\text{CH---CH}-\\ \text{HO} \quad \text{O}\end{array}
$$

Oxidation takes place more readily at the far (13:14) group, and the peroxides formed at this position are more reactive than those formed at the near bond. It is through these latter, more reactive peroxides that polymerization takes place. The beta-elaeostearin compound polymerizes readily and forms hard, fast-drying, varnish-like films. The alpha-elaeostearin compound polymerizes slowly and yields soft, slow-drying films.

[65] R. S. Morrell and E. O. Phillips, *J. Soc. Chem. Ind.*, *58*, 159–162T (1939).
[66] R. S. Morrell and E. O. Phillips, *Fette u. Seifen*, *46*, 541–546 (1939).
[67] R. S. Morrell and H. Samuels, *J. Chem. Soc.*, *1932*, 2251–2254.
[68] R. S. Morrell and W. R. Davis, *J. Soc. Chem. Ind.*, *55*, 2̃3̃⁻ ⸴⸴ ⸴⸴⸴ (1936).

C. Deterioration of Applied Films

1. STRUCTURAL FAILURE

In the case of exterior finishes exposed to sunlight, film failure appears to commonly occur simply through a natural continuation of the process which leads to drying of the film originally. In other words, failure may be attributed to a too advanced state of polymerization. According to this view, so long as the paint retains a sufficient amount of liquid oil to act as a plasticizer it remains tough and flexible. After the liquid portions have largely polymerized to a solid form, however, the film becomes brittle and readily cracks and peels away. A similar cracking occurs in varnished surfaces but with a lesser tendency for the film to become nonadherent. Advanced polymerization is undoubtedly assisted to a large degree by the activating influence of ultraviolet light from the sun. A close correlation has been observed between the accelerated weather resistance of a variety of finishes and the quantity of ultraviolet light absorbed by solutions of the films.[27]

In the ideal drying oil, therefore, the first or the "drying stage" of polymerization will be short; the second or "deteriorative stage" will be prolonged. Although various means may be employed for accelerating the drying process, opportunity for inhibiting later polymerization is limited. To some extent late polymerization may be minimized by properly balancing the relative proportions of reactive and nonreactive fatty acids in the oil. The popularity of linseed oil as a drying oil in the past is attributed to its desirable balance in this respect. In varnishes and other heat-treated products, the cooking operation may produce nonreactive, plasticizing compounds, as mentioned previously.

2. DETERIORATION FROM ACTION OF WATER OR ALKALI

The ability to withstand exposure to water or alkali without swelling, wrinkling, and eventually disintegrating is important in certain finishes. An affinity for water and alkali is clearly linked with the presence in the film of free hydroxyl groups and acidic groups resulting from oxidation, either in air drying or in a prior manufacturing operation. Tung oil and other conjugated acid oils take up much less oxygen than ordinary oils in the process of forming gels, hence their resistance to water or alkali is decidedly superior. Films formed from oils partially polymerized by heat treatment are superior to films in which gelation has been brought about solely by oxidation polymerization. Baked finishes are usually more resistant than those which are air-dried.

Varnishes compounded with phenolic resins, which are particularly ... stability in the presence of water or alkali, likewise pro-

duce films which develop relatively little acidity upon aging.[46] It has been suggested[46] that this property of the phenolics is related to the well-known antioxidant action of many phenolic compounds.

The original acidity of a coating material has no particular bearing on the much greater degree of acidity developed on air drying, and, in fact, the latter is not associated with any considerable amount of hydrolysis of glycerides, but arises from the oxidation of unsaturated fatty acid radicals.[46]

3. Discoloration

A phenomenon of considerable practical significance in the deterioration of oil films is that of "yellowing." The tendency of oil films to develop a yellow or brownish color with age is in more or less direct proportion to their degree of unsaturation. Oils which contain little of any fatty acids more unsaturated than linoleic (soybean oil, poppyseed oil, dehydrated castor oil, etc.) are relatively free from this defect. It is, of course, most noticeable in white paints and enamels, and is favored by the presence of basic pigments.

It appears to be generally agreed that yellowing is in some way connected with the presence of keto groups in adjacent positions in the fatty acid chain:

$$X-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-Y$$
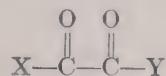
The above group is in itself chromophoric; Elm and Standen[69] proved by synthesis of the respective compounds that diketostearic acid is yellow, whereas ketohydroxystearic acid is colorless.

According to the views of Morrell and Phillips,[66] the yellow substance is probably a metallic compound formed from the diketone, of the formula:

$$X-\overset{}{\underset{\overset{\|}{O}}{C}}-\overset{}{\underset{\overset{|}{OM}}{C}}=CH-Y$$
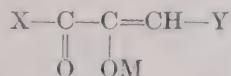
where M may be any basic substance as for example, a basic pigment.

More recently, it has been suggested by Elm[70] that the chromophores are of the type: —CH=CH—CO—CH=CH—CO—CH=CH—, resulting from the oxidation of the active methylene groups in linoleic and, more particularly, linolenic acid, without disturbance of the double bond system. Such a mechanism is consistent with the fact that yellowing is

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[69] A. C. Elm and G. W. Standen. *Ind. Eng. Chem.*, *24*, 1044–1045 (1932)
[70] A. C Elm. *Ind. Eng. Chem.*, *41*, 319–324 (1949).

seldom associated with any evidence of structural deterioration in the film, or even with loss of gloss.

It is conceivable that the colored compounds may have a cyclic structure. The strong yellow color developed in nondrying fats which have become partially oxidized and are then treated with an alkali has been attributed[71,72] to the presence of quinoid compounds formed by the condensation of two diketone molecules:

$$
\begin{array}{c}
\text{O} \\
\parallel \\
\text{X}-\text{C}-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-\text{CH}_2-\text{Y} \\[2em]
\text{O} \\
\parallel \\
\text{X}'-\text{CH}_2-\text{C}-\overset{\parallel}{\underset{\text{O}}{\text{C}}}-\text{Y}'
\end{array}
\quad\longrightarrow\quad
\begin{array}{c}
\text{O} \\
\parallel \\
\text{C} \\
\text{X}-\text{C}\diagup\diagdown\text{C}-\text{Y} \\
\text{X}'-\text{C}\diagdown\diagup\text{C}-\text{Y}' \\
\text{C} \\
\parallel \\
\text{O}
\end{array}
\quad + \quad 2\,\text{H}_2\text{O}
$$
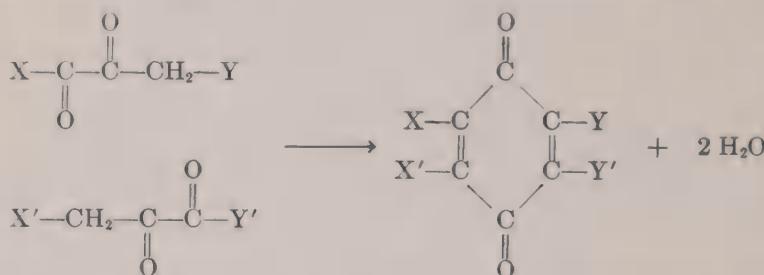
Yellowing does not occur in a perfectly dry atmosphere or at low temperatures.[73] It cannot be due to impurities in the oil, as pure trilinolenin yellows badly.[73,73a] It is favored by irradiation from the red portion of the visible spectrum, but is prevented by exposure to ultraviolet light,[73] hence is chiefly noticeable in white or light-colored interior finishes.

D. Materials

The materials used in making paints, varnishes, enamels, printing inks, and other protective and decorative coatings of an oil-base type may be divided into the following categories: (a) drying oils, (b) resins, (c) pigments, (d) thinners or solvents, (e) dryers, and (f) other miscellaneous ingredients. Detailed consideration will be given here only to the drying oils and to other constituents in their relation to the properties and reactions of the drying oils, inasmuch as the treatment of other materials, for example, pigments, constitutes a complex matter going far beyond the limits of oil and fat chemistry.

Of the true drying oils, only linseed oil, soybean oil, dehydrated castor oil, fish oils, tung oil, and oiticica oil are at present used in quantity by the American industry. Perilla oil, an imported oil used considerably in the past, has been in very short supply for some years, and such minor drying oils as poppyseed oil, hempseed oil, safflower oil, and walnut oil are used only in very small amounts. Semidrying or nondrying oils such as sunflower, corn, cottonseed, untreated castor, and even coconut oil

[71] E. A. Prill, Oil & Soap, 19, 107–109 (1942).
[72] O'Daniel and L. B. Parsons, Oil & Soap, 20, 72–74 (1943).
A. C. Elm, and R. H. Wien, Ind. Eng. Chem., 22, 772–776 (1930).
Eng. Chem., 23, 881–887 (1931).

have been consumed in increasing quantity in recent years in the manufacture of alkyd resin products and a few other synthetic coatings, where they function more as plasticizers than in a drying role.[74] With the augmented use of complex products compounded with the aid of synthetic resins and higher polyhydric alcohols, acids from tall oil are becoming of increased importance in the protective coating field. The consumption of various oils in 1947 is shown in detail in Table 91B.

TABLE 91B

FACTORY CONSUMPTION (THOUSANDS OF POUNDS) OF DIFFERENT FATS AND OILS IN MANUFACTURE OF PAINTS AND OTHER FINISHES AND PRINTING INKS IN UNITED STATES IN 1947[a]

Oil	Paints	Printing inks
Castor oil	32,776	526
Coconut oil	509	—
Corn oil	8	—
Cottonseed oil	38	4
Fish oil	34,201	209
Marine mammal oils	36	8
Lard and rendered pork fat	—	29
Linseed oil	349,262	19,336
Neatsfoot oil	3	8
Oiticica oil	9,339	143
Palm oil	5	—
Peanut oil	—	3
Perilla oil	26	7
Rapeseed oil	3	0
Soybean oil	89,491	1,119
Tallow, inedible, and greases	22	141
Wool grease	38	143
Tung oil	68,968	1,397
Other vegetable oils	4,527	8
Total	*589,252*	*23,072*

[a] U. S. Dept. Agr., *Agricultural Statistics, 1948.*

A point of particular interest is the manner in which modern methods of synthesis and chemical modification have been used to produce for commercial use a wide variety of modified drying oils that were not available to the paint and varnish manufacturer of an older period. A recent and excellent review of the modified drying oils and their points of strength and weakness, based upon the laboratory examination of twenty commercial products, has been published by Houston, Gallagher, and Bolley.[74a]

[74] Castor oil, for example, is a common plasticizer for nitrocellulose coatings.
[74a] G. W. Houston, E. C. Gallagher, and D. S. Bolley, *J. Am. Oil Chem. Soc. 26,* 244–249, 267–271 (1949).

1. UNMODIFIED DRYING OILS

Much of the oil used in the protective and decorative coatings industry consists of unmodified drying oils, *i.e.*, oils whose glycerides are not essentially altered by processing treatment. Unmodified oils may be treated for the removal of nonoil impurities, or may have dryers or other materials added, but are to be distinguished from oxidized, polymerized, and other modified oils which have undergone treatment which involves a separation or reaction of their glycerides.

Raw linseed oil, and to a lesser extent soybean and other oils are extensively used in paints and vehicles for the wet grinding of pigments.

Raw grinding oils are generally acid-refined and bleached. The lighter grades of linseed oil, which are in demand as vehicles for pigments of the lightest and most delicate shades, may have Lovibond colors as low as 20 yellow and 2.0 red, although the color of most grinding oils is in the neighborhood of 35 yellow and about 6.0 red. Soybean grinding oils are generally slightly lighter in color than linseed oil.

The free fatty acid content of grinding oils is somewhat variable. An extremely low acidity in the oil is for most purposes considered neither necessary nor desirable. A certain degree of reaction between the pigments and the free acids will produce a coating of metallic soaps upon the pigment particles, which aids in wetting the pigment and maintaining it in a dispersed condition. On the other hand, excessive reactivity between the pigment and the oil may cause livering in the paint. The optimum degree of acidity in the oil depends upon the reactivity of the pigment. Oils of low acidity, with an acid value of 1 to 2, are preferred for grinding zinc oxide and lithopones. Oils for grinding white lead pastes may have acid values as high as 12 to 16. The acid value of average grinding oils is between about 4 and 6.

Varnish and enamel oils, as well as much of the oils destined for use in paints, are alkali-refined, to produce a low acidity in the oil. For most purposes it is desirable for these oils to be substantially neutral, although a moderately low acid value (1 to 3) is sometimes preferred for special purposes, for example, where the oil is to be compounded with certain synthetic resins.

(a) Refining and Related Treatment

For the production of the highest grade varnish oils, drying oils are generally refined with caustic soda, by a process similar to that employed in the manufacture of edible oil products. Alkali refining completely removes the free fatty acids present in the crude oil, removes all phos-

phatides and mucilaginous materials, and also produces a lighter colored oil than other methods of refining. It is a relatively expensive treatment, however, as it involves a considerable refining loss.

In drying oils which are intended to be used in paints rather than varnishes, the free fatty acids which are naturally present in crude oils are not necessarily objectionable. In fact, in some cases a considerable free fatty acid content in the oil is actually desirable. In paints which contain basic metallic pigments there will be some degree of reaction between the pigments and the free fatty acids of the oil, which will produce a coating of metal soaps upon the surface of the pigment particles. This coating is an aid to the wetting of the pigment in the grinding process. It promotes dispersion of the pigment and inhibits flocculation and settling in the finished paste or paint.

On the other hand, the presence of phosphatides and mucilaginous materials is objectionable in all drying oils. Oils containing these substances "break" when heated rapidly to 550° to 600°F., i.e., they deposit their impurities in the form of flocculent particles. The presence of "break material" is, therefore, inadmissible in any oil which is to be heat-bodied. The presence of "break materials" in a paint film also appears to have a deleterious effect upon the durability of the film, because of their tendency to wash out under the influence of the weather. In addition, they function as antioxidants and retard the drying of the oil. For this reason, an effort is always made to remove phosphatides and gums as completely as possible, even from oil which is not to be subsequently refined. Prolonged storage and settling in storage tanks is an effective means of removal, as the phosphatides gradually become hydrated and separate from the absorption of moisture from the air. In modern practice, however, it is common to accelerate the process by steaming or water washing of the oil. Solvent-extracted soybean oil is often hydrated in the final stage of removing the solvent (page 601), with subsequent separation of the gums by centrifugation. Finally, regardless of the method of separation, the oil is usually mixed with a small proportion of diatomaceous earth, and filtered.

Where chemical treatment other than alkali refining is resorted to for the removal of "break material" in paint oils, the usual refining agent is sulfuric acid, which, when properly used, dehydrates and precipitates the impurities without any considerable action upon the oil itself.

Both linseed and soybean oils which are intended for paint and varnish manufacture are quite commonly "refrigerated," i.e., artificially chilled and filtered for the removal of traces of dissolved waxes. The removal of waxes is said to be particularly important if the oil is to be used in baked finishes, which are otherwise subject to pitting.

The bleaching of drying oils is almost invariably accomplished by means of a bleaching earth, preferably of the acid-activated type, with or without the accessory use of a bleaching carbon. Bleaching of paint and varnish oils by chemical agents is not considered good practice because of the deleterious effect of such agents upon the glycerides of the oil.

Fish oil is almost invariably heat-treated before it is used in paints, to improve its drying properties and to destroy its fishy odor. Fish oil is normally somewhat higher in free fatty acid content than crude vegetable oils, and is usually alkali-refined for use in paints and allied products. It must also be refrigerated or "cold-cleared" (page 872) not for the removal of waxes, but for the removal of "stearine" or solid glycerides, before it is in a suitable form for use in paints or varnishes. The character of the films formed by fish oil depends to a large extent upon the thoroughness with which the refrigeration process is carried out. Fish oil paints are in general inclined to be soft and tacky, due to the high content of saturated fatty acids in the oil. Careful refrigeration to remove the bulk of the more highly unsaturated glycerides will effect a marked improvement in the hardness of the films.

(b) Use of Addition Agents

Formerly, it was necessary to distinguish between raw linseed oil and so-called "boiled" linseed oil, which was oil that had been heated to permit the incorporation of metallic dryers. Now, the driers are usually prepared in the form of a concentrated solution of a metal soap, which is added to the oil along with other constituents of the paint or other product when the latter is compounded.

There is a considerable sale, to varnish manufacturers, printing ink manufacturers, and other oil bodyers, of so-called "catalytic" fact-bodying oils. These consist of alkali-refined linseed or soybean oils to which have been added a small amount of a polymerization catalyst (see page 902); they are said to body in 50–70% of the time of corresponding untreated oils.[75]

(c) Tall Oil

Tall oil is classified here with drying oils, although it is actually a mixture of rosin acids and nonconjugated unsaturated fatty acids. With the recent availability of polyhydric alcohols and a variety of oil-reactive resins, it has become an important new material for protective coating manufacture.

[75] Konen, *Oil & Soap, 21*, 202–204 (1944).

2. Modified Drying Oils

(a) Heat-Polymerized Oils

Heat-polymerized drying oils, or "stand oils," are extensively used in the manufacture of varnishes, enamels, printing inks, and lithographic varnishes, and are also used to some extent in paints, for the improvement in gloss and leveling properties that they contribute.

In the older heat-polymerization processes, in which the oil was heated in open, direct-fired kettles, the oil underwent a considerable amount of oxidation. In modern practice, drying oils are often heat-bodied without access to the air, either under a vacuum or underneath the protection of an atmosphere of carbon dioxide or other inert gas. Oils so bodied are light in color and low in acidity, and are said to be particularly superior to the older stand oils in their resistance to moisture in the applied films. Heat bodying accompanied by oxidation apparently produces greater amounts of hydrophilic substances in the oil than does bodying without access to air.

During the heat-bodying process, polymerization is controlled by means of viscosity determinations on the oil. For ordinary analytical and control purposes, viscosity is determined by the air-bubble method at 25°C. (77°F.) against a standard set of Gardner-Holdt tubes[76] and expressed on the Gardner-Holdt scale. The relationship between Gardner-Holdt viscosities and viscosity in absolute units is shown in Table 92.

Oils may be bodied to any viscosity up to near gelation, according to their anticipated use. Accompanying the change in viscosity during bodying are alterations in the iodine value, acidity, refractive index, saponification value, specific gravity, acetyl or hydroxyl value, etc. Some of these alterations are the natural result of polymerization; others are due to the accumulation of heat degradation products. For detailed information relative to the effect of heat polymerization on the physical and chemical characteristics of different oils, the reader is referred to Chapter XXII and to the original publications of Caldwell and Mattiello[77] (linseed oil), Sorensen, et al.[77] (tung and oiticica oil), Gerkens and Kildare[78] and Von Mikusch[79] (dehydrated castor oil), Work et al.[80] (menhaden oil), and the

[76] H. A. Gardner and G. G. Sward, *Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors.* 10th ed., Institute of Paint and Varnish Research, Bethesda, Md., 1946. See also American Oil Chemists' Society, *Official and Tentative Methods.* Tentative Method Ka 6-48.

[77] B. P. Caldwell and J. Mattiello. *Ind. Eng. Chem.,* 24, 158–162 (1932). S. O. Sorensen, C. J. Schumann, J. H. Schumann, and J. J. Mattiello, *Ind. Eng. Chem.,* 30, 211–215 (1938).

[78] J. F. Gerkens and V. A. Kildare, quoted in *Protective and Decorative Coatings.* Vol. III, J. J. Mattiello, ed., Wiley, New York, 1943, pp. 82–83.

[79] J. D. Von Mikusch. *Ind Eng. Chem.,* 32, 1061–1069 (1940).

[80] L. T. Work, C. Swan, A. Wasmuth, and J. J. Mattiello. *Ind. Eng. C   28,* 1022–1024 (1936).

Los Angeles Paint and Varnish Production Club[81] (sardine oil). Although there is some tendency for oils to increase in acidity during heat bodying, it is possible to produce a high-viscosity product from alkali-refined linseed oil, with an acid value not greater than about 3–4. There is little tendency for tung oil to become more acid during heat bodying. Bodied linseed oil with a Gardner-Holdt viscosity of Z-4 is produced commercially with a Lovibond color no greater than 35 yellow, 3.0 red.

TABLE 92

COMPARISON BETWEEN VISCOSITIES ON GARDNER-HOLDT SCALE AND ABSOLUTE VISCOSITIES

Gardner-Holdt viscosity	Absolute viscosity, stokes	Gardner-Holdt viscosity	Absolute viscosity, stokes
A	0.50	S	5.00
B	0.65	T	5.50
C	0.85	U	6.27
D	1.00	V	8.84
E	1.25	W	10.70
F	1.40	X	12.9
G	1.65	Y	17.60
H	2.00	Z	22.7
I	2.25	Z-1	27.0
J	2.50	Z-2	36.2
K	2.75	Z-3	46.3
L	3.00	Z-4	63.4
M	3.20	Z-5	98.5
N	3.40	Z-6	148.0
O	3.70	Z-7	388.0
P	4.00	Z-8	590.0
Q	4.35	Z-9	855.0
R	4.70	Z-10	1066.0

In the bodying of oils for inclusion in pigmented products, the character and general desirability of the oil is not determined exclusively by its viscosity, but is also influenced to some extent by the conditions under which bodying is carried out. The reason for this is that oils processed at different temperatures and with different degrees of oxidation will vary in their surface-active properties, even though their viscosities may be the same. Consequently, they will wet and deflocculate or flocculate the pigments to different degrees, with consequent effect on the physical properties of the product. The relationship between processing conditions in oil bodying, and wetting in pastes prepared from the bodied oils and various pigments, has been the subject of an extensive investigation by

[81] ... Angeles Paint and Varnish Production Club, *Natl. Paint, Varnish Lacquer* ... *No. 546*, 263–271 (1937); *Am. Paint J.*, *22*, 22–24 (Oct. 30, 1937).

Mattiello and Work[82] (see also General References for the chapter, footnote 1).

Tung oil or other conjugated acid oil which has been heat-bodied in the usual way is subject to the phenomenon known as "gas checking" when exposed to an atmosphere of reducing gases. Since industrial finishes are often baked in gas-fired ovens which permit access to the products of combustion, the oil used in these must be "gas-proofed" by heating to a high temperature. Since tung oil polymerizes and gels so readily that it is not often bodied at a temperature above about 450°F., whereas gas proofing requires a much higher temperature, special equipment is required which will bring the oil very rapidly to 650–700°F., and then quickly cool it.

Some heat treatment is considered neccessary for perilla oil before it is used in protective coatings, to eliminate its tendency to "crawl".

For further information on heat-bodied oils and the heat bodying process reference may be made to Chapter XXII.

(b) Blown or Oxidized Oils

Blown or oxidized oils are prepared by aerating drying oils at a temperature of 200–250°F., for several hours. As oxidation progresses, the viscosity of the oil rises, as in heat bodying, and the specific gravity increases, approaching a value of 1.0 in the heavier blown oils.

Since blown oils have many of the characteristics of heat-polymerized oils, but are processed at temperatures within the range of ordinary steam heating, blowing represents a cheap and relatively easy method of increasing the body of an oil. However, blown oils produce less resistant films than heat-bodied oils, due to their greater content of hydroxyl groups, etc. Also, their solubility in mineral spirits and other solvents is limited. For some purposes the properties of blown oils are unobjectionable, or even desirable. Because of their high surface activity, blown oils are sometimes valuable for mixing with other oils to promote pigment wetting in paints and enamels. They are also used in the manufacture of oilcloth, patent leather, oiled fabrics, and lithographic varnishes, especially the heavier grades of the latter. Blown oils are generally somewhat darker in color and higher in free fatty acid content than heat-polymerized oils of equivalent viscosity. Blowing serves to reduce the objectionable odor of fish oils.

(c) Dehydrated Castor Oil

The dehydration of castor oil depends upon the removal of the hydroxyl group and an adjacent hydrogen atom from ricinoleic acid, in the form of

[82] J. J. Mattiello and L. T. Work, Natl. Paint, Varnish Lacquer Assoc. No. 502, 31–138 (1936). In this connection see also the discussion of heat b   1 relation to wetting of pigments by J. J. Mattiello. i   Coatings, Vol. III, Wiley, New York, 1943,   45–86

TABLE 93

ANALYSIS OF DEHYDRATED CASTOR OILS AND FATTY ACIDS[a]

Analysis	Oil[b]								
	A	B	C	D	E	F	G	H	I
Acid value	1.8	2.6	4.4	13.1	17.0	1.55	3.4	4.8	195.9
Saponification value	190.4	190.0	192.7	190.9	194.2	192.0	191.9	191.6	197.3
Iodine value (Hanus)	155.5	147.1	143.8	157.0	152.9	—	—	—	165.2
Iodine value (Wijs)	141.2	—	—	145.8	—	137.6	117.9	115.1	153.0
Diene value (Kaufmann)	21.4	15.4	15.5	21.9	17.8	17.6	12.7	12.7	26.5
Acetyl value	13.5	14.3	24.8	16.1	19.1	10.6	6.7	9.2	1.2
Viscosity (Gardner)	F-G	H	K	E-F	P	M	Z3	Z2-Z3	A
Color (Hellige)	1-2L	1	2-3L	2L	1-2L	2L	2L-2	1L-1	12Y-1.3R[c]
Specific gravity at 25°C	0.9305	0.935	—	—	—	0.9365	0.9505	—	0.903
Hexabromide value	0.0	—	—	—	—	—	—	—	0.0
Moisture, %	0.0	—	—	—	0.0	0.0	0.0	—	0.45

[a] G. W. Priest and J. D. von Mikusch, *Ind. Eng. Chem.*, **32**, 1314-1319 (1940).

[b] A = typical analysis of a raw dehydrated castor oil made directly from castor oil, type 1; B = sample of a raw dehydrated castor oil made directly from castor oil, type 2; C = sample of a raw dehydrated castor oil, type 3; D = sample made in laboratory according to Münzel's patent; E = sample of European oil made by Scheiber process, type 4; F = typical analysis of a varnish oil (slightly bodied) made from raw oil of type 1; G = typical sample of a heavy-bodied oil made from raw oil of type 1; H = sample of heavy-bodied oil of different origin, type 5;1 I = typical sample of a distilled fatty acid made commercially for the manufacture of alkyd resins from raw oil of type 1.

[c] Lovibond color.

water, to form 9:10, 11:12-octadecadienoic acid:

$$
\begin{array}{ccccc}
13 & 12 & 11 & 10 & 9 \\
H & H & H & H & H \\
| & | & | & | & | \\
CH_3(CH_2)_4C & -C & -C & -C & =C(CH_2)_7COOR \longrightarrow \\
| & | & | & & \\
H & OH & H & &
\end{array}
$$

$$
\begin{array}{ccccc}
13 & 12 & 11 & 10 & 9 \\
H & H & H & H & H \\
| & | & | & | & | \\
CH_3(CH_2)_4C & -C & =C & -C & =C(CH_2)_7COOR + H_2O \\
| & & & & \\
H & & & &
\end{array}
$$
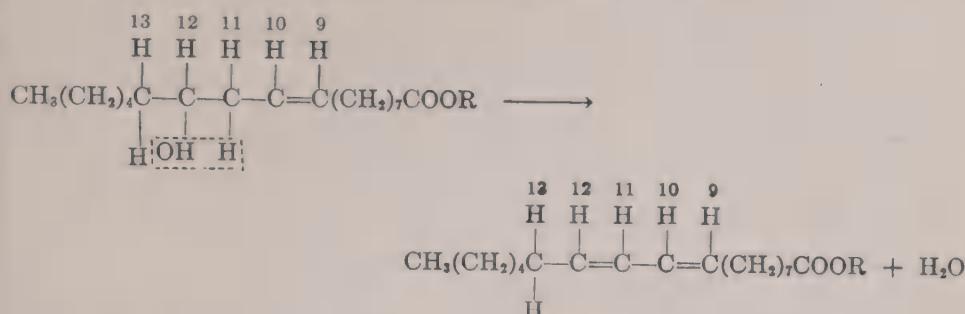
This acid has conjugated double bonds, and thus is similar to the elaeo-stearic acid of tung oil except that it contains two, rather than three double bonds. Dehydrated castor oil has, therefore, to a considerable extent the properties of tung oil.

It is also possible for dehydration to take place by removal of hydrogen from the 13th carbon atom, rather than the 11th, as indicated above, to form ordinary 9:10, 12:13-linoleic acid. Priest and Von Mikusch[83] have made a careful study of the composition of various laboratory- and com-

TABLE 94

COMPOSITION OF COMMERCIAL DEHYDRATED CASTOR OIL, IN COMPARISON WITH ORIGINAL OIL[a]

	Castor oil[b]	Dehydrated oil
Saturated acids, %	0.3	0.5– 2.5
Hydroxy acids, %	87.8	3 – 8
Oleic acid, %	7.2	7.5–10.5
9:10, 12:13 Linoleic acid, %	3.6	59 –64
9:10, 11:12 Linoleic acid, %	0	17 –26

[a] G. W. Priest and J. D. von Mikusch, *Ind. Eng. Chem.*, *32*, 1314–1319 (1940).
[b] Composition as reported by H. K. Dean, *Utilization of Fats*. Chemical Pub. Co., New York, 1938.

mercially prepared samples of dehydrated oil. Contrary to the claims of Scheiber,[84] they conclude that dehydration is never complete (there is always a residue of hydroxy acids), and that in all cases the production of unconjugated linoleic acid considerably exceeds that of the conjugated form. Analyses of various samples of both unbodied and bodied dehydrated oils, as well as dehydrated castor oil acids, as reported by these authors, are detailed in Table 93. From these analytical data, they esti-

[83] G. W. Priest and J. D. Von Mikusch, *Ind. Eng. Chem.*, *32*, 1314–1319 (1940).
[84] J. Scheiber, *Farbe u. Lack, 1928*, 518–520; *1929*, 153–154; *1930*, 513–514, 524–525; *1936*, 570; *Angew. Chem.*, *46*, 643–647 (1933). Ger. Pats. 513,309 (1930); 13,540 (1930); 555,496 (1932); Brit. Pat. 316,538 (1928); U. S. Pats. 1,979,495 1,942,778 (1934).

mate the composition of dehydrated castor oil, in comparison with ordinary castor oil, to be as indicated in Table 94.

A more recent report by Terrill,[84a] indicates that the content of conjugated isomers in modern unbodied dehydrated castor oils generally approaches 30%. The percentage is of course lower in bodied oils. Apparently some of the oils examined by Priest and Von Mikusch were incompletely dehydrated, or partially bodied. Their estimates of conjugation were, furthermore, made by an indirect method which is less reliable than modern spectrophotometric analysis.

According to Terrill,[84a] the common commercial grades of dehydrated castor oil include one unbodied grade and several bodied grades, of which one of Z-2 to Z-4 viscosity is the most used. A.S.T.M. Tentative Specification D-961-48-T for dehydrated castor oils is shown in Table 94A.

TABLE 94A

A.S.T.M. SPECIFICATIONS FOR DEHYDRATED CASTER OIL[a]

Properties	Unbodied	Bodied
Viscosity at 25 °C	F+ to J−	Z-2+ to Z-4−
Specific gravity, 15.5/15.5 °C	0.930–0.941	0.950–0.970
Acid number	6 max.	6 max.
Saponification number	188–194	188–194
Iodine number (Wijs)	130–145	100 min.
Color (Gardner 1933)	6 max.	7 max.
Gel time, min. at 600 °F	145 max	63 max.
Set-to-touch time, hrs. (with 0.3% lead, 0.03% cobalt dryer)	2.5 max	1.4 max.
Refractive index at 25 °C	1.4805–1.4825	1.4860–1.4885

[a] A.S.T.M. Standards on Paint, Varnish, Lacquer, and Related Products, 1949.

In many of its properties, such as drying time, rate of polymerization when heated, and resistance to water and alkalies in varnish films, dehydrated castor oil is intermediate between linseed oil and tung oil. It is said to produce films which are softer than those of linseed, perilla, or tung oils, but of superior elasticity. Because of its lack of triply unsaturated acids, its resistance to yellowing is outstanding. The properties of dehydrated castor oil, in comparison with various natural drying oils, are discussed at length by Priest and Von Mikusch.[85]

Dehydrated castor oil has attained extensive use as a replacement for tung oil in the manufacture of quick-drying and water-resistant varnishes and enamels. It has also been used to some extent in most other varieties

[84a] R. L. Terrill. J. Am. Oil Chem. Soc., 27, 477–481 (1950).
[85] W. Priest and J. D. Von Mikusch. in Protective and Decorative Coatings. J. Mattiello, ed., Wiley, New York, 1941. pp. 115–150.

of drying oil products, including paints, oiled fabrics, linoleum, patent leather, and printing inks and lithographic varnishes.

All of the dehydrated castor oil produced in the United States is apparently made by some variation of the Ufer process,[86] rather than by the original method of Scheiber[84] i.e., dehydration is carried out on the glycerides rather than the separated fatty acids of the oil.

Castor oil dehydrated by the Münzel process,[87] which involves both dehydration and dehydrogenation, is said to contain a triply unsaturated conjugated acid, with double bonds in the 9:10, 11:12, and 13:14 positions, respectively. This oil has been produced commercially in Europe, under the trade name of Trienol. According to Blom,[88] this product will gel in 1.5 minutes at 280°C. (536°F.), and dries more rapidly than natural tung oil. However American workers[83] have been unable to substantiate the claims of some of the Münzel patents, and there appears to be some question of the authenticity of samples of oil distributed under the Trienol name and claimed to be of synthetic origin.[89]

(d) Isomerized Oils

The isomerized oils which have appeared on the market in the United States under the trade names of Conjusoy, Conjulin, etc., are prepared by treating oils containing linoleic and linolenic acids in such a manner as to induce a shift in the double bonds of these acids to conjugated positions:

These oils, like dehydrated castor oil, are substitutes for tung oil.

Apparently, the isomerized oils so far produced are made from soybean and linseed oils by the alkali isomerization process described by Bradley and Richardson.[90] This process consists essentially of reacting the fatty acids of the oil with an excess of aqueous alkali solution at a high temperature (425–450°F.) and a correspondingly elevated pressure, acidulating the resulting soap to recover the isomerized acids, and re-esterifying the latter with glycerol. Laboratory isomerization of soybean oil by this method produced simultaneous yields of doubly and triply unsaturated conjugated acids as high as 43.8% and 2.2%, respectively, as estimated

[86] H. Ufer (to I. G. Farbenindustrie), Ger. Pats. 529,557 (1931); 561,290 (1932); U. S. Pat. 1,892,258 (1932).
[87] F. Münzel, Swiss Pat. 193,931 (1938).
[88] A. V. Blom, in Oil and Colour Chemists' Assoc., *Varnish Making*. Chemical Pub. Co., New York, 1940, pp. 31–39.
[89] T. P. Hilditch and M. L. Meara, *Chem. & Ind.*, *1946*, 158.
[90] T. F. Bradley and D. Richardson, *Ind. Eng. Chem.*, *34*, 237–242 (1942).

from ultraviolet adsorption spectra data. Corresponding yields of these acids from laboratory-isomerized linseed oil were as high as 35.2% and 9.7%, respectively.

The isomerized oils have been sold in a bodied form, some degree of heat polymerization presumably being unavoidable in the process of re-esterification.

The catalytically isomerized oils, as compared with other drying oils, are somewhat slower in drying, and form softer films than might be expected from their content of conjugated acids, which greatly exceeds that of dehydrated castor oil. It is believed this is due to the formation of isomers which polymerize less readily than naturally occurring acids. However, it is said that isomerized soybean oil is roughly equivalent to dehydrated castor oil in drying properties, and that isomerized linseed oil is superior to dehydrated castor oil, although inferior to tung oil. The water resistance of isomerized linseed oil films has been reported to be higher than those of tung oil,[91] although their alkali resistance is less than that of tung oil films.

Of the various processes claimed for the isomerization of drying oils without recourse to alkali treatment or hydrolysis of the glycerides, the nickel–carbon catalytic method described by Radlove et al.[92] is of greatest present interest, although it does not appear to have been reduced as yet to commercial practice. Although by catalytic isomerization it has been possible to produce oils with 30–34% total conjugation from soybean or linseed oils, the performance of these oils, like that of the alkali-isomerized oils has been to some degree disappointing. Presumably because of the production of isomers subject to rapid thermal polymerization but relatively slow in air drying,[30] the oils have not yielded films greatly superior in hardness, drying time, or durability to films from the nonisomerized oils, even though they are considerably more reactive in the processes of heat bodying or varnish cooking.[64,93]

(e) Fatty Acid Esters of Higher Polyhydric Alcohols

Of the various polyhydric alcohols capable of yielding fatty acid esters of greater functionality than glycerides, only pentaerythritol[94-96] and sorbitol[95,97,98] are at present sufficiently cheap and sufficiently satis-

[91] J. E. Good, *Can. Paint & Varnish Mag.*, 17, 5, 7, 17, 23, 25 (Feb., 1943).
[92] S. B. Radlove, H. M. Teeter, W. H. Bond, J. C. Cowan, and J. P. Kass, *Ind. Eng. Chem.*, 38, 997–1002 (1946).
[93] L. B. Falkenburg, A. W. Schwab, J. C. Cowan, and H. M. Teeter, *Ind. Eng. Chem.*, 38, 1002–1009 (1946).
[94] H. Burrell, *Oil & Soap*, 21, 206–211 (1944); *Ind. Eng. Chem.*, 37, 86–89 (1945).
[95] J. C. Konen, E. T. Clocker, and R. P. Cox, *Oil & Soap*, 22, 57–60 (1945).
[96] Heyden Chemical Corp., *Pentek Resins*. New York, 1948.
[97] D. Brandner, R. H. Hunter, M. D. Brewster, and R. E. Bonner, *Ind. Eng. Chem.*, 37, 809–812 (1945).
[98] Powder C⸺ *Atlas Sorbitol in Protective and Decorative Finishes*, Wil-

factory on other accounts to have attained any considerable use in protective coatings. Of the two, pentaerythritol is the more useful, since its structure (of four primary hydroxyl groups) permits it to be more readily esterified. When sorbitol is reacted with fatty acids the inner hydroxyl groups tend to interact, to produce inner ethers.

While the pentaerythritol esters of linseed oil fatty acids body and dry more rapidly than the natural oil, the chief utility of this alcohol appears to be in the utilization of less saturated fatty acids such as those from soybean oil or tall oil.[99] Soybean oil pentaerythritol esters are reported[99] to be virtually equivalent to natural linseed oil in either paints or varnishes. In alkyd resins the use of pentaerythritol in place of glycerol permits the use of less unsaturated acids or smaller proportions of fatty acids or oil without the sacrifice of durability or drying properties. The pentaerythritol alkyds are also said to be more compatible with modifying melanine or urea resins of limited solubility.

Pentaerythritol   Sorbitol
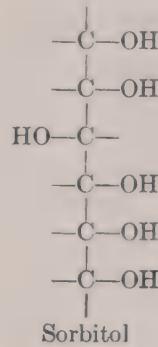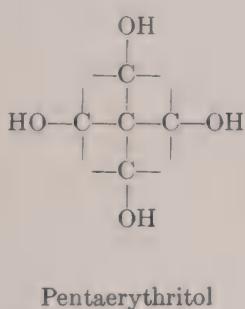
Sorbitol is said[98] to be particularly useful, not as the sole alcohol in a coating composition, but as a modifying agent to be used in connection with glycerol, pentaerythritol, or other polyhydric alcohols. The use of more than one alcohol in compounding a synthetic gum or resin often permits the attainment of desirable combinations of melting point, viscosity, and solubility that are impossible with a single alcohol.

The increasing demand for polyhydric alcohols in protective coatings will doubtless lead to the economical production of other useful members of this class of compounds.[100]

(f) Fractionation Products

Fractionation processes are of particular interest in the utilization of soybean oil, which is deficient in over-all unsaturation, and fish oils, which are highly unsaturated, but nevertheless contain undesirably large proportions of saturated acids.

[99] D. S. Bolley, Ind. Eng. Chem., 41. 287–294 (1949).
[100] H. Wittcoff, J. Am. Oil Chem. Soc., 26, 157–161 (1949); J. P. G..... .....nd K. M. Gordon, Ind. Eng. Chem., 42, 1591–1594 (1950).

A commonly used fractionation method for fish oils is that of so-called "solvent segregation" (page 880), which involves heat bodying of the oil, followed by liquid–liquid extraction with ketones, higher alcohols, or other polar solvents.[101,102] As limited polymerization involves only the less highly saturated glycerides, and as the polymerized portion of the oil is relatively insoluble in the solvent, whereas the unpolymerized portion is freely soluble, this produces an extract in which the more saturated glycerides are concentrated, and a residue of superior drying properties. Because of the fractionation of glycerides achieved, and also because the extraction washes out all heat-degradation products of low molecular weight, the solvent-segregated fish oils are said to be outstandingly superior in resistance to water, alkali, and natural weathering, and to produce phenolic varnishes with characteristics approaching those of tung oil varnishes.[101]

Solvent segregation has also been applied to bodied linseed oil, in the manufacture[103] of the so-called "Tekaols."

Fish oils, such as sardine or menhaden, are particularly suitable materials for fatty acid fractionation, since most of their saturated fatty acids contain 14 to 16 carbon atoms, whereas their highly unsaturated acids containing three or more double bonds per molecule, are principally C_{20} and C_{22} acids. An excellent separation of the two classes of acids may be obtained by fractional distillation. Some improvement in the drying properties of soybean or other vegetable oils may be effected by the same process, since the saturated acids of these oils consist principally of palmitic (C_{16}) acid, which is more volatile than the unsaturated C_{18} acids.

Fractionated vegetable oil and fish oil fatty acids, as well as different grades of triglycerides from fractionated fish oil acids, have been placed on the market by one American manufacturer under the trade name of "Neo-Fats." Characteristics of some of these products, as reported by the manufacturers,[104] are listed in Table 95. Their manufacture and uses have been discussed by Stingley.[105] They are suitable for virtually all purposes for which drying oils are used. Neo-Fat No. 190 triglyceride is particularly recommended for admixture with dehydrated castor oil as a substitute for tung oil in the manufacture of spar varnishes and other water-resistant and quick-drying finishes. Used alone, it produces unduly hard and brittle films. This oil, which has an iodine value of about 205, is more highly unsaturated than any natural drying oil.

Other products of the same manufacturer include Neo-Fat 17, the mixture of highly unsaturated fatty acids and polymerized glycerides

[101] W. H. Mattil, Oil & Soap, 21, 197–201 (1944).
[102] O. M. Behr (to Vegetable Oil Products Co.). U. S. Pat. 2,239,692 (1941).
[103] Rossmann, Angew. Chem., 50, 246–248 (1937).
[104] Neo-Fat: New Fatty Acids and Oils for Industrial Purposes, Armour and Co.
[105] Stingley, Ind. Eng. Chem., 32, 1217–1220 (1940).

from which Neo-Fat 170 is produced by esterification, and fractionated tall oil products of low rosin acid content (6–12%).

<div align="center">TABLE 95</div>

<div align="center">CHARACTERISTICS OF NEO-FATS (PRODUCTS OF FATTY ACIDS FRACTIONATED BY DISTILLATION)[a]</div>

	3-R	19	170	190
Number.................				
Type...........	Fatty acids	Fatty acids	Triglyceride	Triglyceride
Source..................	Veg. oil	Fish oils	Fish oils	Fish oils
Mean molecular weight....	281.0	305.0	—	—
Neutralization value.......	198.0	184.0	—	—
Saponification value.......	—	—	160.0	177.0
Iodine value, Wijs........	140.0	235.0	170.0	205.0
Acid value..............	—	—	8.0	6.0
Titer, °C................	19.0	20.0	—	—
Specific gravity at 25°C....	—	—	0.980	0.950
Viscosity, at 25°C., poises..	—	—	heavy	2.0
Unsaponifiable matter, %..	0.3	0.5	—	—
Color....................	nil	pale	dark	pale
Odor..................	mild	good	—	—
Approximate composition of fatty acids, %:				
Oleic..................	39.5	10	—	10
Linoleic...............	59.0	—	—	—
Linolenic...............	nil	—	—	—
C_{20} unsaturated.........	—	90	—	90
C_{22} unsaturated........	—	—	—	—
Saturated..............	1.5	—	—	—

[a] *Neo-Fat: New Fatty Acids and Oils for Industrial Purposes.* Armour and Co.

Liquid–liquid extraction, by either the furfural or liquid propane processes, appears to be an advantageous method for treating soybean oil or fish oils for use as drying oils, although up to now little oil fractionated by this method has been commercially available. Representative analytical data on liquid–liquid extraction products are given in Chapter XXI. It will be noted that the extraction technique effects a much more extensive fractionation of fish oils than the "cold-clearing" process which is more commonly applied to these oils. Sardine oil, for example, will yield a substantial cut with an iodine value as high as 240 (from oil of 185 iodine value originally), whereas even the best commercial cold-cleared oils are not higher than 195–200 in iodine value.

<div align="center">(g) <i>Maleic Oils</i></div>

The manner in which conjugated fatty acids and their ester react at moderate temperatures with maleic acid or maleic anhydride form

"adducts," has been outlined on page 421. At somewhat more elevated temperatures, i.e., above about 200°C., nonconjugated fatty acids and esters likewise form an addition product, presumably according to the following typical reaction:[106]

$$
\begin{array}{cccccc}
\text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\
| & | & | & | & | & | \\
-\text{C}-\text{C}-\text{C}=\text{C}-\text{C}-\text{C}- \\
| & | & & & | & | \\
\text{H} & \text{H} & & & \text{H} & \text{H}
\end{array}
\quad + \quad
\begin{array}{c}
\text{H}-\text{C}=\text{C}-\text{H} \\
| \quad\quad | \\
\text{O}=\text{C} \quad \text{C}=\text{O} \\
\diagdown \text{O} \diagup
\end{array}
\quad \longrightarrow
$$

$$
\begin{array}{cccccc}
\text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\
| & | & | & | & | & | \\
-\text{C}-\text{C}-\text{C}=\text{C}-\text{C}-\text{C}- \\
| & | & & & | & | \\
\text{H} & \text{H} & & & \text{H} & \text{H} \\
& & & & & | \\
& & & & & \text{H} \\
& & & & & | \\
& & & \text{H}-\text{C}-\text{C}-\text{H} \\
& & & \quad | \quad\quad | \\
& & & \text{O}=\text{C} \quad \text{C}=\text{O} \\
& & & \quad \diagdown \text{O} \diagup
\end{array}
$$
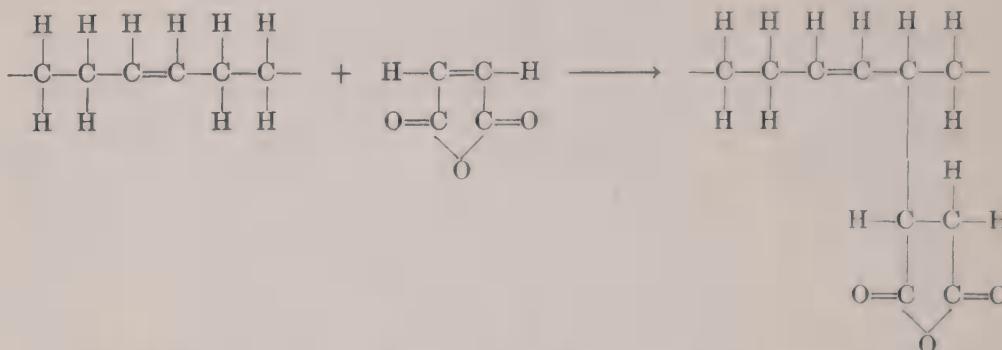
So-called maleic oils or "maleinized oils" are one of the important new synthetic drying oil products. From the above it will be recognized that maleinization constitutes a ready means of inserting free acid groups into the middle of an unsaturated acid chain, and thus of increasing the *functionality* of the fatty acid. The utility of this is obvious. Soybean oil, tall oil, or other slow polymerizing oils, when treated with 5–10% of maleic anhydride and sufficient pentaerythritol or other polyhydric alcohol to esterify the free acid, will polymerize rapidly. The presence of the maleic group tends to make the oil more compatible with nitrocellulose. Larger proportions of maleic anhydride yield resins of varying degrees of hardness.

Neutralizing the maleic group with ammonia or other alkali makes maleic oil adducts water-soluble, and, peculiarly, upon drying the solubilized oils largely lose their hydrophilic properties and develop quite good water resistance. For this reason, one of their most important present uses is in the formation of the new oil-base water-dispersible paints.[107]

3. RESINS AND COPOLYMERIZING MATERIALS

The resins used in varnishes and other coatings are for the most part high polymers which are capable of reacting with drying oils under the influence of heat, to form copolymers which are faster drying, and give harder, glossier, or more durable films than the drying oils alone. A few synthetic resins apparently do not so interact, but simply dissolve in the oleaginous vehicle, and eventually contribute to the formation of a solid film through a normal thermosetting process. In the case of shellac and

[106] W. G. Bickford, P. Krauczunas, and D. H. Wheeler, *Oil & Soap*, 19, 23–27 (1942).

[107] T. Clocker, U. S. Pats. 2,188,882–890 (1940); 2,262,923 (1941); 2,275,843 and 2,28... nd 2,286,466 (1942).

other so-called spirit varnishes, drying oils may be absent from the vehicle altogether.

The use of resins in combination with oils is very old, dating back to the ancient Egyptians. Until quite recently, the available resins were natural products, consisting of complex polymers formed by the sap exuded from trees. Now, a great variety of synthetic resins are available, and these have to a large degree supplanted the natural resins in varnish manufacture.

In recent years the total consumption of resins in protective coatings in the United States has approached one-half the total tonnage of drying oils.

(a) Natural Resins[108]

Of the various natural resins, the harder, rarer, and more desirable varieties, such as Kauri, Congo, Manila, Pontianak, and Boea, are fossil materials, formed by trees that are no longer living. Although synthetic resins are now available which surpass any natural resins with respect to the hardness, durability, or chemical resistance of the varnish, it is still considered that natural resin varnishes give films that will take a higher polish, and are more suitable for fine furniture, etc.

The fossil resins, because of their age and their advanced degree of polymerization, are not soluble as such in hot oils, and when cooked in varnishes must be "run" or subjected to a prior step of heat degradation at a very high temperature.

So-called "recent" resins, obtained from living trees, include Dammar, East India, and Batu. They are soluble not only in hot oil, but also in common volatile organic solvents, and are now perhaps more used in spirit varnishes than in oleoresinous vehicles. Rosin may be considered a variety of recent resin. Large quantities are consumed in protective coatings. Rosin alone is quite soft, hence it is ordinarily used in a modified form, i.e., hardened by reaction with lime, with a polyhydric alcohol, with maleic anhydride, or combined with phenolic resins. The glycerol ester of rosin, or "ester gum," is a common constituent of varnishes, either alone (usually with tung oil) or in combination with harder and more expensive resins. There is some use of rosin esters of glycol (Flexalyn) and of pentaerythritol. Maleic- or phenolic-modified ester gum is now used in considerably greater volume than the pure gum.

Natural asphalts, e.g., Gilsonite, are commonly employed as the res-

[108] See P. O. Powers, Chapter 7, C. L. Mantell, Chapter 8, and A. J. Wittenberg and J. Saphier, Chapter 10, in Protective and Decorative Coatings, Vol. I, J. J. Mattiello, ed., Wiley, New York, 1941; A. A. Albert, Chapter 7, and G. T. Sohl, Chapter 8, in Paint and Varnish Technology, W. von Fischer, ed., Reinhold, New York, 1948; C. L. Mantell, C. W. Kopf, J. L. Curtis, and E. M. Rogers, Technology of Natural Resins, Wiley, New York, 1942.

inous component in black varnishes or "japans." Shellac, the dried exudation of a sap-sucking East Indian insect, is an important natural resin, which, however, is seldom used except in spirit varnishes. The natural lacquers or "lacs" of Oriental origin are of a resinous nature, but are not used in modern manufactured coatings, although cashew shell "oil" a chemically similar material, finds considerable use in specialty products, such as insulating varnishes.

(b) Phenolic Resins[109-112]

The first synthetic resins to be used successfully in varnishes, and still among the most important, were phenol-formaldehyde condensation products closely related to the well-known Bakelite plastics. When first introduced, ca. 1913, unsubstituted phenol was used in their preparation, and it was necessary to modify them with rosin or a rosin ester to make them oil-soluble. Later (about 1928), 100% phenolic oil-soluble resins were made available through the use of phenol with ortho- or para-substituted alkyl or aryl groups (e.g., butyl, amyl, or phenyl).

Two entirely different types of resins are used in the coating industry. The most commonly used product is obtained with the aid of an acid catalyst, which produces a permanently oil-soluble and thermoplastic material suitable for use in air-drying finishes. An alkaline catalyst yields a thermosetting material which becomes insoluble in oil if the reaction is carried to completion. In an oil-soluble form it is heat-reactive in the oil, hence it cannot be cooked in the varnish batch in the usual way, and is chiefly used in baking finishes. The heat-reactive material also finds use as an adjunct for use with slow-cooking oils and ester gum or other cheaper and less reactive resin.

Phenolic resins, like natural resins, appear actually to react with drying oils, to produce what is essentially a copolymer of oil and resin. They reduce the cooking time of varnishes markedly, and yield quick-drying finishes, yet inhibit the slow after-polymerization which leads to deterioration of the applied films.[111]

The first "four-hour" varnishes were products of tung oil and modified phenolic resins, and it is still considered that the phenolics exhibit their particular virtues to the best advantage in combination with tung oil or other conjugated acid oils.

[109] See R. J. Moore and W. R. Catlow, Jr., Chapter 12, in *Protective and Decorative Coatings*, Vol. I. J. J. Mattiello, ed., Wiley, New York, 1941.
[110] R. B. Waters, Chapter 11, in *Paint and Varnish Technology*, W. von Fischer, ed., Reinhold, New York, 1948.
[111] R. C. Shuey, Chapter 6A, in *Protective and Decorative Coatings*, Vol. III. J. J. Mattiello, ed., Wiley, New York, 1943.
[112] O. Powers, *Synthetic Resins and Rubbers*, Wiley, New York, 1943. R. S. Mor . . . od., *Synthetic Resins and Allied Plastics*, 2nd ed., Oxford University Press, Lon . . . 43.

While phenolic resin varnishes are superior in a number of respects to the older products compounded with natural resins, their outstanding advantage is in resistance to water and alkalies, and consequent increased durability in outdoor use. It has been stated[110] that before the advent of 100% phenolic resins, varnishes were considered good if they would withstand 15 minutes in boiling water or 30 minutes in dilute alkali, whereas the use of these resins (with tung oil) at once increased the boiling water resistance to 7 hours and the alkali (5% sodium hydroxide) resistance to 24–48 hours. Because of their tendency to yellow with age, they are seldom used in white enamels or other light finishes.

Phenolic resins of the heat-reactive type, with or without short oil modification, and used in the form of a solution in organic solvents, constitute one of the most durable and chemically resistant protective coatings known. They are widely used in coating the interior of cans, drums, tanks, and miscellaneous industrial equipment, and in exacting marine applications.

In recent years the consumption of the various pure phenolic resins has been rapidly increasing, but is still exceeded in volume by rosin or ester gum modified phenolics. The latter are in particular demand as an ingredient of furniture varnishes.

(c) Alkyd Resins[112-114]

Alkyd resins are polymers produced by the esterification of a polyhydric alcohol with a polybasic acid. In the present commercial products the polyhydric alcohol is usually glycerol, although pentaerythritol is finding increasing use. Phthalic acid, in the form of the anhydride, is much the most widely used acid, although there is a limited use of other dibasic acids, such as maleic and fumaric.

The manner in which glycerol molecules may be linked through the medium of phthalic acid may be represented as follows:
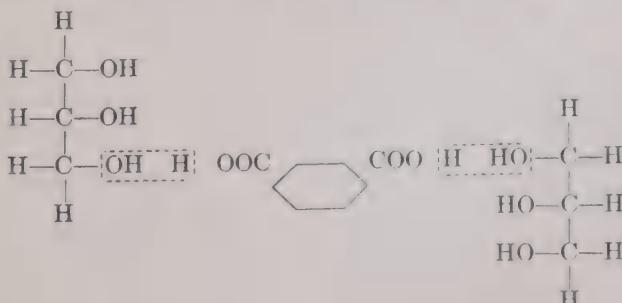
[113] C. S. Ferguson and J. E. Sellers, Chapter 13, in *Protective and Decorative Coatings*, Vol. I, J. J. Mattiello, ed., Wiley, New York, 1941.
[114] C. L. Levesque, Chapter 9, in *Paint and Varnish Technology*, W. von Fischer, ed., Reinhold, New York, 1948.

Inasmuch as glycerol is trifunctional and phthalic acid bifunctional, there is ample opportunity for cross linking, to form a rigid three-dimensional structure; these two reactants alone quickly form a brittle, nonfusible, and nonsoluble mass. To produce tough and flexible polymers suitable for protective coatings, the resin is "oil-modified," *i.e.*, a certain proportion of the glycerol hydroxyl groups is esterified with fatty acids. Oil modification is, in effect, a means of controlling the functionality of the glycerol or other polyhydric alcohol (see page 418), by tying up hydroxyls with a monobasic group incapable of further esterification. By varying the amount of oil used, the degree of esterification polymerization may be varied at will, and products may be obtained with a continuous gradation of properties. If very little oil is incorporated, the product will, of course, be little different from the insoluble 100% alcohol-acid polymer referred to above. If it consists largely of oil, its properties will approach those of the oil alone. Products of intermediate composition will have properties intermediate between those of the two.

In addition to limiting the degree of cross linking, the presence of the long and relatively flexible fatty acid chains has a plasticizing effect. If the fatty acids are unsaturated and have drying properties, they will also interact with one another under the influence of heat or oxidation, and a true copolymer will result.

The highly important factor of the degree of oil modification is often expressed in terms of the so-called *alkyd ratio*, which is defined as the per cent by weight of glyceryl phthalate in the material, calculated upon the basis of a hypothetical stoichiometric combination between glycerol and phthalic anhydride.[114,115] Most of the alkyd resins used in coatings have alkyd ratios between about 65 and 18.[114] Short-oil alkyds, with alkyd ratios ranging from about 50 to 65, are most used for baked finishes on automobiles and household refrigerators, stoves, washing machines, etc., which were at one time usually given a ceramic coating. They are often made with nondrying oils, such as coconut oil or raw castor oil (because of the resistance of these to yellowing) and are commonly hardened by the addition of small amounts of alkylated urea or melamine resins. The short-oil alkyds, particularly if modified with castor oil, are to some degree compatible with nitrocellulose lacquers, and are often blended with the latter.

Long-oil alkyds, which are always based upon drying oils, with an alkyd ratio of about 31, are principally used in brushing enamels for interior or exterior architectural work where fast drying, durability, and good color and gloss retention are desired.

Medium-oil alkyds, with alkyd ratios of about 39 to 45,[115] constitute

‘ Beavers, ‘ . . *Eng. Chem.*, 41. 738–740 (1949).

an intermediate all-purpose class, which have good air-drying properties, but greater gloss and durability than the long-oil product. Unlike the short-oil alkyds, they tolerate a variety of thinners sufficiently well to be thinned readily to brushing or spraying consistency. They are usually modified with either linseed or soybean oil. They may be made with quite satisfactory baking characteristics, and they will tolerate the addition of melamine hardeners. Maximum impermeability to water and exterior durability is said to be realized at an alkyd ratio of about 50.[116]

Unlike most other resins, alkyd resins are not manufactured in a form suitable to be cooked with oil to produce a varnish or enamel vehicle, but are made by reacting oil (or fatty acids), glycerol, and phthalic anhydride together in a single batch. If oil is used, it and the glycerol are first reacted to form an equilibrium mixture of mono-, di-, and triglycerides, and free glycerol, after which reaction is continued with the addition of phthalic anhydride. Since nothing more than straightforward esterification is involved, with a minimum of side reactions, it would appear that the composition of a given product should be susceptible to mathematical analysis. For theoretical treatments of the subject, reference may be made to the publications of Hönel,[117] Savard and Diner,[118] Kienle, Petke, and van der Meulen,[119] Lynas-Gray,[120] Goldsmith,[121] Levesque,[114] and Earhart.[116]

Alkyd resins from pentaerythritol attain their greatest usefulness in the long-oil form, where the increased functionality of the alcohol permits the attainment of comparable hardness and durability with greater proportions of oil than in a glycerol product. Sorbitol or other polyhydric alcohols should, of course, yield the same advantage. Some proportion of glycerol may be used if increased flexibility is desired at a given oil length.

It is claimed[116a] that alkyd resins made from styrenated fatty acids have superior drying properties and chemical resistance.

Alkyd resins are sold in the United States under the trade names of Glyptal, Rezyl, Aroplaz, Duraplex, Beckosol, etc.

(d) Other Oil-Reactive Materials

A very widely used resin consists of the maleic anhydride adduct of ester gum (Amberol, Lewisol, Beckacite, etc.), or of the pentaerythritol

[116] K. A. Earhart, *Ind. Eng. Chem., 41*, 716–725 (1949).
[116a] N. R. Bhow and H. F. Payne, *Ind. Eng. Chem., 42*, 700–703 (1950).
[117] H. Hönel, *Paint Oil Chem. Rev., 91*, No. 23, 19–26 (1931).
[118] J. Savard and S. Diner, *Bull. soc. chim., 51*, 597–615 (1932).
[119] R. H. Kienle and F. E. Petke, *J. Am. Chem. Soc., 61*, 2268–2271 (1939); *62*, 1053–1056 (1940). R. H. Kienle, P. A. van der Meulen, and F. E. Petke, *ibid., 61*, 2258–2268 (1939).
[120] J. I. Lynas-Gray, *Paint Technol., 11*, 129–140 (1946); *12*, 7–10 (1947).
[121] H. A. Goldsmith, *Ind. Eng. Chem., 40*, 1205–1211 (

ester of rosin (Pentalyn). Resins of somewhat similar structure and properties are prepared by forming the same adduct of terpenes or unsaturated turpentine fractions (Petrex, Piccolyte, etc.), or of cyclopentadiene (Carbic resin). All of the maleic resins are characterized by pale colors and good color retention, which make them suitable for use in light finishes.

Although in some cases it has not been clearly established whether a given resin actually enters into reaction with a drying oil, to form an oil copolymer, it appears that certain products from unsaturated petroleum fractions, such as Velsicol and Stanco A, are certainly to be classed as oil-reactive. Recently,[122] the protective coatings industry has manifested considerable interest in copolymers of styrene and drying oils, and a number of commercial products have appeared on the market.

A comprehensive review, covering the theory, manufacture, and utilization of styrene and cyclopentadiene copolymers has recently been published by Hovey.[122a]

(e) Resins of the Non-Oil Reactive Type

Resins that are common ingredients of oleoresinous coatings, but which react independently of the drying oil in the vehicle, include alcohol-modified *urea* and *melamine* resins which, as mentioned previously (page 445), find their chief use as hardeners for alkyds; and *coumarone-indene resins* (Cumar, etc.), which are used chiefly in aluminum paints, concrete coatings, and other specialty products in which their naturally dark color is not disadvantageous. A number of other resins may find their way into nitrocellulose lacquers and other solvent or spirit finishes in company with glyceride oils, but their utilization forms no proper part of the subject of drying oil technology, and will not be considered here.

4. DRYERS[123,124]

Almost all oleoresinous coating materials contain metallic "dryers" to promote solidification of the applied films. Dryers have quite a pronounced effect—a film of raw linseed oil, for example, will require 3 to 4 days to dry, whereas the incorporation of dryers may reduce this time to as little as 4–12 hours.

Presently used dryers are virtually all soaps of lead, manganese,

[122] D. H. Hewitt and F. Armitage, *J. Oil Colour Chem. Assoc.*, **29**, 109–128 (1946); H. M. Schroeder and R. L. Terrill, *J. Am. Oil Chem. Soc.*, **26**, 153–157 (1949). H. M. Hoogsteen, A. E. Young, and M. K. Smith, *Ind. Eng. Chem.*, **42**, 1587–1591 (1950).
[122a] A. G. Hovey, *J. Am. Oil Chem. Soc.*, **27**, 481–491 (1950).
[123] C. A. Klebsattel, Chapter 22, in *Protective and Decorative Coatings*, Vol. I, J. J. Mattiello, ed., Wiley, New York, 1941.
[124] B. Elliott, Chapter 16, in *Paint and Varnish Technology*, W. von Fischer, ed., ...old, 1948.

cobalt, iron, calcium, or zinc, with rosin, naphthenic, or fatty acids. Formerly, the different metals were commonly incorporated into drying oils by prolonged heating of the oils with metal oxides, to produce so-called "boiled" oils. Now, a dryer concentrate is usually prepared separately, and "precipitated" dryers, made by double decomposition of sodium soaps of the acids and an aqueous solution of a metal salt, have largely replaced "fused" dryers, obtained by reacting the acids directly with the metal oxide or hydroxide. The commercial production of dryers has recently been described in detail by Kastens and Hansen.[125]

Although the dryers are pro-oxidants, their action in drying oils is not altogether similar to the action of metallic pro-oxidants in nondrying oils. They are said to increase the rate of oxygen absorption after the induction period ends, as well as to shorten the induction period, and they appear to accelerate polymerization by direct carbon-to-carbon bridging, inasmuch as drying is attained with less oxidation in their presence than without.

Of the various metals, cobalt is much the most powerful in its drying action. However, since cobalt tends to produce rapid surface hardening with a large amount of oxidation, which interferes with uniform through-curing of the film, it is seldom used alone. Lead promotes slow but uniform drying, accompanied by a minimum amount of oxidation, whereas manganese is intermediate in its action. With respect to the relative effectiveness of the three metals, it is stated[123] that one part of cobalt is approximately equivalent to 8 parts of manganese, which is equivalent to 40 parts of lead. In general, it is considered that a combination of metals produces more satisfactory drying than any single metal. For ordinary exterior house paints and similar finishes a lead–manganese combination is more or less standard (about 0.02–0.05% manganese and 0.4–0.6% lead, as metals). In interior paints, and varnishes and enamels, cobalt is usually used to the amount of 0.005–0.02% with somewhat less lead (0.2–0.4%), and manganese is often omitted.

In alkyd resin finishes and other modern coatings the compatibility of the dryer with the vehicle must be considered. On this score, cobalt is good, but lead is relatively poor; hence cobalt is often used in combination with zinc or calcium, which are relatively ineffective dryers alone, but which effectively replace lead in modifying the surface drying characteristics of cobalt, and produce satisfactory through-drying. With a given metal, the solubility of a dryer depends a great deal upon the acid used in forming the metal soap.[126] Their superior solubility characteristics, as well as their greater stability in concentrate form, has contributed

[125] M. L. Kastens and F. R. Hansen, *Ind. Eng. Chem.*, *41*, 2080–2090 (1949).
[126] H. Bruson and O. Stein, *Ind. Eng. Chem.*, *26*, 1268–127⁷ ⁻34).

to the growing preference for metal naphthenates as dryers over the older "resinates" and "linoleates." Because of the color of its salts, manganese is not considered a good dryer for white enamels, whereas cobalt is entirely satisfactory.

Iron is relatively ineffective in air drying, but is a good dryer for baked finishes, and is often used in baked japans, where the dark color of its compounds constitutes no disadvantage.

5. THINNERS[127]

Organic solvents or thinners are used to reduce the viscosity of coating materials so that they can be applied uniformly and conveniently. They are used in almost all oleoresinous paints, varnishes, and enamels, and occasionally in printing inks; they are particularly important components of varnishes and other quick-drying coatings in which the vehicle is caused to undergo a considerable amount of polymerization before the coating is applied.

Formerly turpentine was the standard thinner for paints, but in recent years it has been largely replaced by naphthas derived from petroleum, which consist predominantly of straight chain hydrocarbons. The widespread use of synthetic resins and the growing complexity of modern quick-drying finishes has imposed exacting requirements upon thinners with respect to solvency, evaporation rate, etc., and these requirements have been met by an increasing use in oleoresinous finishes of hydrocarbons of the saturated cyclic (naphthene) and unsaturated cyclic (aromatic) types, derived from petroleum or coal tar.

The solvent power of a thinner is commonly expressed in terms of the so-called kauri-butanol value, which is determined by making a standard solution of kauri resin in butanol and titrating this solution with the thinner in question to the point where the resin begins to precipitate. The solution will, of course, tolerate a larger amount of a thinner of high solvent power than one of low solvent power. Aromatic solvents are better solvents than naphthenes, which are in turn better than aliphatic hydrocarbons.

In practice, a thinner for any given product must be chosen, not only for its solvency and its efficiency in reducing the viscosity of the vehicle, but also on the basis of the rapidity and completeness with which it is released from the applied coating (either slow or rapid release may be desired), and the condition in which it leaves the coating upon evaporation, as well as its cost. Very often, optimum properties are realized in a mixture of solvents rather than in a thinner composed largely of one compound or one class of compounds. For modern coatings the proper

[127] See Chapters 23–27, in J. J. Mattiello, ed., *Protective and Decorative Coatings,* Vol. I, Wiley, New York, 1941.

choice and compounding of thinners or solvents is a complex subject which cannot be dealt with here.

The amount of thinner to be incorporated in a coating material is determined by the method of application as well as the original viscosity of the nonvolatile vehicle; relatively high viscosities are required for roller coating or brushing, and relatively low viscosities for spraying or dipping. The proportion of thinner in the liquid portion of a prepared product varies from as little as about 10% by weight in some exterior paints to as high as 75% or more in certain dipping preparations.

6. PIGMENTS

Protective and decorative coatings contain pigments primarily to obscure the surface over which they are applied. However, the pigments are by no means chemically inert constituents, and they profoundly influence the serviceability as well as the appearance of applied films, and also properties related to the ease of application of the coatings, and their keeping qualities in packaged form.

White pigments account for a good part of the "hiding power" of many colored coatings, as well as white paints and enamels. None of these pigments is actually opaque; rather, they obscure through their ability to refract and scatter light rays. The hiding power of a (white) pigment in a vehicle is proportional to the square of the difference in refractive index of pigment particles and vehicle; hence true pigments of high refractive index, e.g., titanium dioxide, $n_D = 2.7–2.9$, are to be distinguished from "extenders," e.g., calcium carbonate, $n_D = ca.$ 1.65, whose refractive indices approach that of common vehicles ($n_D = 1.50–1.55$).

For many years white lead (basic carbonates and sulfates) and zinc oxide were the standard white pigments. Lithopone, a synthetic barium sulfate–zinc sulfide pigment, began to become popular in about 1920. Titanium dioxide pigments of very high refractive index and desirable weathering characteristics were introduced in about 1925, and have steadily grown in use since then, usually in combination with other pigments or extenders of lower hiding power. Since titanium dioxide has four to nine times the hiding power of an equivalent weight of lithopone, zinc oxide, or white lead, it may now be considered the most important white pigment, even though on a tonnage basis its consumption is not more than about half that of zinc and lead pigments. Titanium dioxide is produced in two crystal forms, anastase and rutile, of which the latter has a somewhat higher hiding power.

The important extender pigments, which contribute little to hiding, but are added to coatings to produce body, to adjust tints, and even in some cases for improved durability, include magnesium and alu_ m

silicate minerals, calcium carbonate, and calcium and barium sulfates.

Colored inorganic pigments include lead and zinc chromates, cadmium sulfide, chromium oxide, ferric-ferrocyanides (iron blues), and natural ferric oxides. Metallic aluminum powder is a widely used pigment. The important black pigments are carbon products, prepared by the incomplete combustion of natural gas (carbon black) or mineral oils (lamp black). A wide variety of organic dyes or "toners" is used in producing the brilliant colors now demanded in many types of finishes.

Since the plastic properties of a mixed paint depend upon the relative volumes of pigments and vehicle, the weight of a pigment to be used in a given formulation will depend upon its specific volume, or *"bulking value."* Bulking values, in terms of gallons per 100 pounds of pigment vary from about 1.8 for white lead to 6.5 for carbon black. The *"pigment volume percentage"* of different paints and enamels (on the basis of pigments plus nonvolatile vehicle) ranges from as little as about 5% to as much as about 70%.

For detailed information on the involved subject of pigments and toners, one of the standard texts on the subject may be consulted.[128]

7. Miscellaneous Ingredients

For the production of a "flat" finish with naturally glossy coatings, so-called *"flatting agents"* are used. These consist for the most part of insoluble fatty acid soaps of aluminum, calcium, or zinc, which deposit on the surface of the dried film minute, virtually invisible particles capable of scattering light.

Thickening or *suspending agents*, added to inhibit pigment settling and to give specific body characteristics in certain products, include aluminum soaps, limed oils, soya lecithin, and water in the form of a weak soap solution.

In quick-drying finishes a problem is presented by the tendency for a solidified film or skin to form on the surface of the packaged material, particularly in an opened container. *"Antiskinning"* agents[129] of one class are antioxidants which inhibit the formation of such films without materially increasing the drying time of the product. As an example of their action, it has been reported[130] that N-(2-nitroisobutyl)p-toluidine added to a limed rosin–tung oil varnish to the amount of 0.05 g. per 50 ml. has the effect of increasing the skinning time from 1 day to 7 days, without extending the original drying time of 5 hours. Another generally less effective type consists of solvents which apparently inhibit the forma-

[128] For example, J. J. Mattiello, ed., *Protective and Decorative Coatings*, Vol. II. Wiley, New York, 1942.

[129] *Natl. Paint, Varnish and Lacquer Assoc. Circ.* No. 400 (1932).

[130] G. Johnson, *Ind. Eng. Chem.*, 37, 1176–1178 (1945).

tion of a skin through their ability to act as dispersants for polymers.

The wetting and dispersion of pigments in a vehicle is usually controlled by the degree to which free acidity and surface-active products of oxidation are allowed to accumulate in the drying oil portion. However, the addition of synthetic surface-active agents has been recommended.[131]

E. Manufactured Products

While any detailed description of the many types of protective or decorative coating compositions is quite beyond the limitations of this volume, an attempt will nevertheless be made to indicate very briefly the nature, composition, and uses of the more important types. Discussion will be confined to oleoresinous products which are designed to be applied in liquid form, and which dry to form solid films, *i.e.*, to paints, varnishes, printing and lithographic inks, etc. Drying oil products such as linoleum, factice, rubber substitutes, etc., which contain oil in a solid polymerized form, will be discussed in Chapter XIII devoted to miscellaneous oil and fat products.

1. Oil Paints

While the elaboration of modern coating materials has tended to obscure former more or less clear-cut distinctions between different classes of products, the term "paint" is generally taken to include pigmented compositions made up with a vehicle which consists predominantly of unmodified drying oil or oil of low viscosity. Paints are thus to be distinguished from oleoresinous varnishes or enamels, in which the vehicle has been fortified with a resin and has been treated to bring about partial polymerization. They are characterized by relatively slow drying and films that are lacking in hardness and chemical resistance (although not necessarily lacking in durability), in contrast to varnish and enamel films, which are hard and often highly impervious to water, alkalies, and other reagents. Owing to a natural persistence of terms in the language of the trade, many products are still designated as paints which might more properly be called enamels.

Any paintlike product must have a certain degree of body to enable it to form a uniform film which will not sag or run during the drying period. In the case of slow-drying products, it is not sufficient for the applied film to be merely viscous—it must have some degree of plasticity to enable it to withstand the long continued stress of its own weight while drying. Quick-drying coatings, on the other hand, may not flow to a serious extent during the drying period if they are merely sufficiently viscous.

[131] E. K. Fischer and C. W. Jerome, *Ind. Eng. Chem.*, *35*, 336–343 (1943).

If the vehicle in a coating composition is lacking in body, this property must be obtained by the incorporation of a large proportion of pigments; hence in all paints there is a relatively high ratio of pigments to vehicle. Usually the pigments in a paint contribute from about 25% to as much as 50% of the total volume of the pigment–vehicle mixture. Often the amount of pigments required to give the product adequate hiding power is insufficient for proper consistency, and "extender" pigments of low hiding power are added for the sake of the latter property. The ratio of pigments to vehicle employed in different paints is governed by the nature of the surface to be painted, as well as the properties desired in the final paint film. Owing to their high proportion of pigments, the characteristics of paint films are to a large extent dependent upon the nature of the pigments. On the other hand, in the case of enamels, lacquers, or other products which are compounded with a quick-drying vehicle of high viscosity and relatively little pigment, the character of the film is determined largely by the vehicle.

High concentrations of pigments produce a characteristically low gloss or sheen in applied films, hence highly pigmented paints are ordinarily "flat," whereas high gloss is associated with enamels, varnishes, and lacquers, which are either unpigmented or lightly pigmented.

(a) House Paints

Ordinary house paints are usually prepared by mixing a pigment and suitable dryers with a vehicle consisting predominantly of unmodified linseed oil. A small proportion of bodied linseed oil, e.g., 8–10%, of about Q viscosity is often incorporated in the vehicle, since the addition of such an oil improves the durability of the film, and assists in "leveling" or the elimination of brush marks. The amount of bodied oil which it is practicable to use is limited by the adverse effect of such oil on the brushing properties of the paint. Soybean oil and fish oil are used to some extent in house paints, but due to their slow drying properties and the softness of their films, they are almost invariably mixed with a large proportion of linseed oil. Heat-treated perilla oil, tung oil, oiticica oil, and dehydrated castor oil have been used to some extent in house paints, although normally these oils are rather too expensive in comparison with linseed oil to be common ingredients. House paints, when applied in three coats, are ordinarily thinned with a small proportion, e.g., 10–15%, of turpentine or mineral spirits before they are applied, to reduce their consistency, the first or priming coat being thinned to the greatest extent, and each successive coat being thinned less than the one preceding it. Recently the "two-coat" system of house painting[132] has become very popular, and has

L. Browne, *Ind. Eng. Chem.*, *33*, 900–910 (1941).

to a considerable extent replaced the traditional three-coat system. This system involves the use of special paints which form thick coatings and produce in two applications a film equivalent in thickness to that obtained in three applications by the older method. An essential requirement in two-coat work is a priming paint vehicle which does not penetrate deeply into the wood, and which consequently may be highly pigmented. Retention of the vehicle by the pigments is favored by the presence of bodied oils, or any other component which promotes pigment wetting.

Although ordinary house paints are made with a cheaper vehicle than varnishes, enamels, or lacquers, it must not be inferred that they are necessarily inferior in serviceability to the latter products. House paints have certain distinctive properties which make them uniquely suitable for their particular use. In this connection it must be remembered that wood is a highly porous material, and that the properties required in a wood coating are in some respects quite different from those required in a coating material for metals or other nonporous substances. One highly important characteristic of house paints is their appreciable permeability to water vapor. During cold weather there is in a heated house a temperature gradient extending through the walls from the warm, moist air within the house to the cold exterior air. If this gradient is not interrupted by the interposition of a cold air space back of the boards to which paint is applied, condensation of water will take place within these boards to such an extent that they may become saturated. A completely moisture-impermeable coating will cause liquid water to collect at the paint–wood interface, with subsequent detachment of the coating film.[133] Enamels or other products containing varnishes or resins are less permeable to water vapor than ordinary oil paint. They also more readily become embrittled from exposure to oxygen and ultraviolet irradiation, in exterior applications, and hence are inclined to fail through cracking or checking.

Since a house paint is applied but once to a new surface, which may be repainted many times, the ability of a paint to adhere to its own deteriorated films is highly important. In this respect, an ordinary linseed oil paint is outstandingly superior to most other coating materials. The character of the deteriorated film is likewise important, both from the standpoint of adhesion of the new film and the appearance of the old film during the period of deterioration. Good house paints, unlike other coatings, have certain "self-cleaning" properties; there is a tendency for the paint film to chalk off gradually, adherent surface dirt being removed during the process of chalking.

Finally, since house paints are usually applied by means of the brush, their brushing characteristics are of some importance. Paints which contain a high proportion of pigments are more easily brushed out to a uni-

133 J. W. Iliff and R. B. Davis, *Ind. Eng. Chem.*, *31*, 1407–1412, 1446–1450 (1939).

form film than more viscous but less plastic coating compositions.

Certain of the characteristics associated with the relatively expensive varnishes, enamels, etc., are unnecessary or even undesirable in house paints. Very fast drying is of no particular advantage in a product used to paint a house, since it does not speed the over-all painting job, and the slightly greater dust pick-up of a slowly drying surface is inconsequential in a finish lacking a high gloss. Even if it were obtainable, a very high gloss would hardly be desirable in a house paint, since such a finish serves to accentuate minor irregularities of the painted surface, and hence is not particularly pleasing except on very smooth and finely finished surfaces.

Pure white lead was once considered the most desirable pigment for a white house paint. Now, good house paints usually contain anastase titanium dioxide in combination with lead or lead and zinc pigments and an extender material. In addition to its high hiding power, the titanium dioxide contributes to a continued good appearance of the paint coating through its self-cleaning or slight chalking tendency. A pigment volume concentration of about 28–30% is generally considered optimum in the dried paint film. A porous and nonserviceable film results if the amount of pigments is increased above a critical concentration corresponding to that at which the nonvolatile portion of the vehicle is unable completely to fill voids between the pigment particles. Because of the different packing characteristics of different pigments and the tendency of pigment particles to agglomerate to varying degrees according to the wetting power of the vehicle, this critical concentration is quite variable.[133a] Values from about 26 to 47% have been recorded.[133a]

(b) Exterior Trim Paints

For trim work on houses, for finishing commercial structures such as store fronts and gasoline stations, for commercial sign painting, and for other purposes where decorative effects are emphasized, there is a demand for brightly colored paints of high gloss that are nonchalking and capable of retaining their appearance upon exposure to the weather. These exterior "trim" paints are actually enamels rather than paints, usually of a long-oil alkyd type. To insure high gloss, the pigment volume must be held to about 15–20%.

(c) Interior Architectural Paints

The coating materials used for interiors are now usually hardened with at least some proportion of varnish. In many cases they are actually pigmented varnishes or enamels, although in the trade the term "enamel"

[133a] W. K. Asbeck and M. Van Loo, *Ind. Eng. Chem.*, 41, 1470–1475 (1949).

is usually reserved for products which produce a film of high gloss.

To meet the demand for finishes of varying surface appearance, interior coatings are marketed as flat paints, semigloss paints, gloss paints, and enamels. The degree of gloss depends primarily upon the volume of pigment in the film, which is said[134] to vary from about 52.5 to 71.5% in flat paints, from about 33 to 52.5% in semigloss and gloss paints, and from about 20 to 33% in enamels. The pigments used in interior paints are not essentially different from those of exterior paints, except that extenders are less commonly used in the gloss products. Flatting and suspending agents equivalent in amount to 1% or less of the pigments are common ingredients.

(d) Industrial Paints

Industrial paints for such structures as factory and farm buildings, warehouses, smokestacks, tanks, and bridges and other supporting structures, and for railway equipment and ships, are manufactured in a very wide variety of special forms. In general, where the paint is intended to be largely or entirely protective, a vehicle is used which is more or less similar to that of a house paint. Where decorative effects are sought, the characteristics of the paints approach those of the architectural trim paints.

A number of pigments are used in industrial paints which are seldom encountered in any of the types of paint enumerated above. These include red lead, which is a standard ingredient of rust-inhibitive primers for structural steel or similar steel work, metallic aluminum, which is particularly popular in tank and roof paints, and graphite, which is used in smokestack paints.

2. Varnishes and Enamels

Varnishes are of two types, oleoresinous varnishes and spirit varnishes. The former, which is commercially much the more important, comprises products made by partially polymerizing a drying oil at a high temperature with resins, and thinning the resulting product to a usable consistency with a volatile solvent. Spirit varnishes do not contain oils and consist of resins dissolved in a suitable solvent. Enamels are pigmented varnishes.

The outstanding characteristics of varnishes, enamels, etc., and the characteristics which distinguish these products from ordinary oil paints, are their quick-drying properties and the hardness, waterproofness, and usually high gloss of their films.

[134] R. E. Troutman, Chapter 11, in *Protective and Decorative Coatings,* Vol. III. J. J. Mattiello, ed., Wiley, New York, 1943.

Owing to the great variety of drying oils, natural and synthetic resins, and solvents now available to the industry, varnishes and related products are manufactured in extraordinary variety, and are among the most versatile of coating materials. By a suitable choice of raw materials and compounding methods their properties may be varied widely and closely adapted to specific uses. They are universally used as protective coatings for wood or metal surfaces which are subject to abrasion, since paints have poor abrasion resistance, regardless of their ability to withstand weathering. Articles manufactured in large quantities by assembly line methods are almost invariably coated with finishes of the varnish type, because of the ability of such finishes to dry quickly, and to respond to heat treatment during drying. Varnishes or oil modified resins can be made with a resistance to water or dilute alkalies or acids superior to that of any other flexible coating material. Consequently they are now used in applications where ceramic or other nonflexible and difficultly applicable coatings were formerly considered essential. Their flexibility readily lends them to such uses as coating fabrics. Since they can be made highly resistant to both moisture and heat, they are extremely valuable electrical insulating materials.

Owing to the speed with which they dry, they are important ingredients in inks for high-speed, multicolor printing. In addition to their protective qualities, the decorative properties of these coatings are in general superior to those of paints, because of their high gloss and good color retention.

Although tung oil or other conjugated acid oils are generally preferred for varnish making, and in fact may be regarded as more or less indispensable for the production of certain types of varnishes, including those with high water and alkali resistance, there is some use in varnishes of practically all the drying oils. The introduction of highly reactive synthetic resins has made possible the production of varnishes or varnish-like materials from oils of relatively poor drying properties. Thus, for example, soybean oil is extensively used in the manufacture of oil-modified alkyd resins. The influence of different resins on the properties of varnishes in which they are incorporated has been discussed previously in dealing with the different resins that are available.

Varnishes are of short or long "oil length," the length being defined as the number of gallons of oil used in the formula per 100 pounds of resin. Different varnishes vary greatly in oil length, according to the variety of oil and of resin used in their composition, and their intended uses. In general, however, oil length will vary between about 10 and 75 gallons. Since the resins in a varnish are responsible for its hardness and rapid drying properties, whereas the oil imparts flexibility and stability toward deterioration by oxidation, the formulation of a varnish for a particular

purpose depends to some extent upon properly balancing the properties imparted by the two ingredients. The different resins now available differ so widely in their properties, however, that it is hardly possible to make categorical statements relative to the effect of oil length on the character of the product. Thus, for example, varnishes made with natural resins are increasingly durable in exterior applications with increasing oil lengths, whereas a reverse relation is said to hold in the case of phenol-formalde-hyde resin varnishes.[135]

3. WATER-DISPERSIBLE PAINTS

Water paints or "kalsomines," consisting of lime, whiting, china clay, etc., with glue as a binding agent, were widely used for many years as a cheap, nonwashable interior finish. Later, these were somewhat improved by replacement of the glue with casein (in combination with lime) or soybean protein, and by the inclusion in the formula of a small propor-tion of emulsified drying oil.

Whereas the improved paints of the casein type have a fair measure of wearability and washability, it is only with the recent advent of so-called oil emulsion paints that water-dispersible finishes have become available which compare in this respect with conventional oleoresinous products. The emulsion paints offer outstanding advantages to the house-holder in ease and convenience of application and freedom from paint or thinner odor, and they now constitute an exceedingly important trade sales item.

The major oleoresinous component of the first emulsion paints was an alkyd resin; lately, there has been an increasing usage of other oleoresin-ous materials, including particularly maleic-treated oils, which become easily dispersible, and, in fact, to some degree water-soluble in an alka-line emulsion (page 440). In order to realize the particular benefits of this type of paint it is necessary, of course, to make the oil or resin the internal or discontinuous phase. Pigments, similar to those employed in conventional paints, are dispersed in the oil. A very fine emulsion is re-quired, with most of the oil droplets having diameters of the order of one micron or less. For the sake of good package stability, they are marketed in the form of a fairly stiff paste, which is thinned with water (0.5–1.0 gallon per gallon of paste) by the user before application. Preservatives to prevent growth of bacteria or mold are required. Additional ingredients include vegetable gums or other protective colloids, emulsifying and thickening agents, and antifoaming compounds. Casein or other protein material is still used in small amounts in emulsion paints for its ability to maintain dispersion in alkaline emulsions.

[135] R. J. Moore and W. R. Catlow, in *Protective and Decorative Coatings*, Vol. I, J. J. Mattiello, ed., Wiley, New York, 1941.

The emulsion paints dry rapidly by the evaporation of water, followed by oxidation polymerization of the oleoresinous component, which coalesces upon disappearance of the water to form a continuous film. Their use is no longer confined to interior flat work; films of considerable gloss may be produced, and they are sufficiently resistant to water to be readily washed or in some cases even used for exterior painting.

In the formulation of a satisfactory emulsion paint it is essential to produce an emulsion which is stable in the package, which may be easily thinned to a form suitable for application, and which will leave a uniform, nonporous oleoresinous film when the water is released. Obviously, these requirements make the technology of emulsion paints highly involved.[136]

4. PRINTING INKS

Properly speaking, printing inks are not necessarily either protective or decorative coatings. However, they are so similar to paints and varnishes that they are logically placed in the same classification.

Because of the dissimilarity of the different printing processes, and the great diversity of surfaces presented by different papers, etc., a very large number of different inks are required completely to fill the needs of the printing trade. In the words of Fuhrmann et al.,[137] "the technique of ink making consists very largely of detail." For each variety of printing press and each surface to be printed, the ink must be carefully blended to obtain a proper balance among the various factors of flow, adhesion, penetration, speed of drying, etc. Obviously, therefore, the complete technology of inks is highly involved. It will be attempted here merely to indicate the different types of inks, and very briefly outline the composition, characteristics, and uses of printing inks in general.

Methods of printing are divided into three main classes. While inks of quite different characteristics may be employed with presses of a single class, according to the mode of operation of the press, the nature of the surface to be printed, and the kind of printing desired, there are nevertheless certain limitations imposed by the fundamental nature of each process. It is in order, therefore, to consider briefly the three printing methods before proceeding to a discussion of printing inks.

In relief printing the ink is caused to adhere to raised surfaces on the printing plate, from which it is transferred by contact to the paper or other material printed. In gravure or intaglio printing, the design to be printed is indented in the printing plate, rather than raised. The plate is

[136] For a recent review of the chemistry and technology of emulsion paints, see G. M. Sutheim, Chapter 11, in *Protective and Decorative Coatings*, Vol. IV, J. J. Mattiello, ed., Wiley, New York, 1944.

[137] O. W. Fuhrmann, L. O. Buttler, P. F. Duffy, F. G. Schleicher, and J. J. Mattiello, Chapter 21, *Protective and Decorative Coatings*, Vol. III, J. J. Mattiello, ed., Wiley, New York, 1943.

first completely covered with ink, which is then wiped cleanly from the raised surfaces, leaving ink only in the depressions. On contact with the plate, the paper is forced slightly into the depressions, bringing the ink with it as it is removed. In planographic printing, the printing plate has a plane surface, and the design is formed by treating the plate chemically so that portions are easily wetted and ink-repellent, and other portions are water-repellent and ink-receptive. Planographic printing may be conducted in the ordinary manner, or by the offset process. In the latter process, the paper is not placed directly in contact with the plate, but the ink is transferred from the plate to the surface of a rubber "blanket," and from the rubber surface to the paper.

Most typographic printing is done by the relief method, whereas, the principal uses of gravure and planographic (lithographic) printing are for the reproduction of illustrative material.

Some paper stocks, including ordinary newsprint, are so highly absorbent that "drying" of the ink occurs largely by penetration. In printing such paper, the ink does not actually form a film, and the vehicle merely serves as a carrier for the pigment. Most papers, however, are sufficiently sized to be relatively nonabsorbent, so that printing is quite similar to painting, i.e., it involves the application of a thin film which must dry by oxidation, polymerization, or evaporation. Hence many printing inks may be regarded merely as special varieties of oil paints or varnishes. In printing ink films, such properties as hardness, elasticity, durability, waterproofness, etc., are of minor consequence, or in some cases of no consequence at all. The principal purpose of a printing ink is to transfer the design afforded by the printing plate cleanly and adequately to the paper. Most printed material is produced in quantity, by presses operating at high speed, and in some processes of color printing, successive films of ink are applied one over the other. For this reason, the drying properties of inks are almost always of great importance.

The ingredients used for compounding printing inks are in general the same as those employed in the manufacture of paints and varnishes, with two important exceptions. Raw or unbodied oils are seldom, if ever, incorporated in printing inks, and for printing on very absorbent paper stock, where no drying is required, a cheap mineral oil is generally substituted for the fatty oil.

The foundation of printing ink formulation consists of the so-called lithographic varnishes, which actually are heat-bodied oils, usually linseed oils, of varying degrees of body or viscosity. Although a common numbering system is used by different manufacturers for designating the different viscosities of varnish, the specific viscosity associated with each number appears to be subject to some variation. Fuhrmann et al.[137] list twelve different varnishes, numbered from 00000 to 8, with approximate

viscosities ranging from 2.08 poises for No. 00000 to 137.0 poises for No. 5. The Gardner-Holdt[76] standards for lithographic varnishes consist of ten tubes numbered from 000 to 8, omitting No. 7, with viscosities (in stokes) as follows:

No. 000........	1.80	No. 3..........	34.0
No. 00.........	4.80	No. 4..........	62.1
No. 0..........	8.00	No. 5..........	120.0
No. 1..........	14.40	No. 6..........	200.0
No. 2.........	23.50	No. 8..........1250.0	

Varnishes of each body are made in both amber and pale grades, the latter being used as vehicles for the lighter, more brilliantly colored pigments. In the formulation of a printing ink, a single varnish is not generally used alone, but varnishes of different bodies are mixed together, to develop to an optimum degree the properties of fluidity, tack, etc.

Other ingredients of printing inks include blown oils, "burnt" oils, mineral oils, dryers, organic solvents or thinners, natural and artificial resins, pigments, and "compounds." Blown oils are principally used in the manufacture of very heavy-bodied lithographic varnishes. "Burnt" oils are heat-bodied oils which have been prepared by heating the kettle of oil to a temperature above its fire point, then setting fire to its surface and permitting it to burn slowly for several hours. In this manner a product is obtained which is considered to be less "greasy" than ordinary heat-bodied oil. Mineral oils are chiefly used as vehicles for newsprint inks, but may also be incorporated as plasticizers in other vehicles. The pigments employed in the greatest volume in printing inks are somewhat different from those which are most popular with paint manufacturers, and consist principally of carbon and various synthetic organic materials. Most of the resin used in the manufacture of oleoresinous varnishes for printing inks is rosin or ester gum, although alkyds and other synthetic resins also find use in these materials. "Compounds" are waxy materials such as soap, tallow, vegetable waxes, etc., introduced in minor amounts in printing inks to modify the tackiness of the product.

In the following paragraphs the principal types of printing inks are briefly described.

News inks, as mentioned previously, contain no fatty oils, being prepared with a mineral oil vehicle. However, all other inks, with the exception of a few varieties of the lacquer or spirit varnish type, employ drying oils in their composition. *Cylinder press inks* are relatively slow-drying, thin-bodied products which dry to a considerable extent by penetration, like news inks. Their vehicles consist of a composite of thin- and medium-bodied lithographic varnishes. Cylinder press inks formulated for multicolor process printing must be carefully adjusted with respect to

tack and drying properties, in order to permit satisfactory overprinting of the various colors. In a series of such inks the consistencies of the various members of the series must be correlated; each of the successive colors must have less tack than the preceding color, in order that rupture of the ink film will occur in the top layer,[138] or so that each color will be "trapped" by the preceding color. These properties are adjusted by the proper blending of light-, medium-, and heavy-bodied lithographic varnishes, and suitable inclusion of dryers and compounds. Some of these inks must necessarily dry quite rapidly, and some are considerably heavier in body than ordinary cylinder press inks. *Job printing inks* are compounded from medium- and heavy-bodied lithographic varnishes, and often contain an oleoresinous varnish. They are used for miscellaneous printing on sized, relatively nonabsorbent paper, and hence dry to a large extent by oxidation and polymerization. *Bond inks* are still heavier than job printing inks and are made with a vehicle consisting of medium- and heavy-bodied lithographic varnishes and oleoresinous varnishes. They are used for the printing of letterheads, etc., on high-grade bond paper, and dry largely by oxidation and polymerization. *Bookbinders' inks* are very heavy, almost to the point of pastiness. They are prepared with heavy oils and varnishes, and are used for printing the covers of cloth-bound books. All of the preceding inks are used in printing by the relief method.

The inks used in connection with gravure or intaglio printing processes are of three principal types. *Plate inks* contain a vehicle consisting of a "burnt" plate oil, mixed with oleoresinous varnishes. They are used for very fine printing, as of bonds, certificates, currency, etc. *Embossing inks* are in effect fast-drying pigmented oleoresinous varnishes. They are used for printing the more expensive stationery, business cards, etc., to produce a characteristic raised design of high gloss and hardness. *Rotogravure inks* are compounded from lithographic and oleoresinous varnishes, with sufficient thinner to produce a very fluid, fast-drying product.

Lithographic inks are products of relatively viscous body compounded from various lithographic varnishes, and in some cases oleoresinous varnishes. The intricate nature of the lithographic process makes the formulation of this type of ink particularly exacting. In addition to very definite requirements in regards to fluidity, adhesiveness, and cohesiveness, it is essential that lithographic inks have a minimum tendency to emulsify with the aqueous dampening solutions used to make portions of the plate water-repellent.

[138] H. Green, *Ind. Eng. Chem., Anal. Ed., 13,* 632–639 (1941).

F. Manufacturing Operations

1. COOKING OF VARNISHES AND RESINS

(a) Varnish Manufacture

The early varnish kettles were simply portable, open, hand-stirred pots, usually made of copper or Monel metal, which were designed to be moved on or off fire pits with the aid of wheels or monorail conveyors.
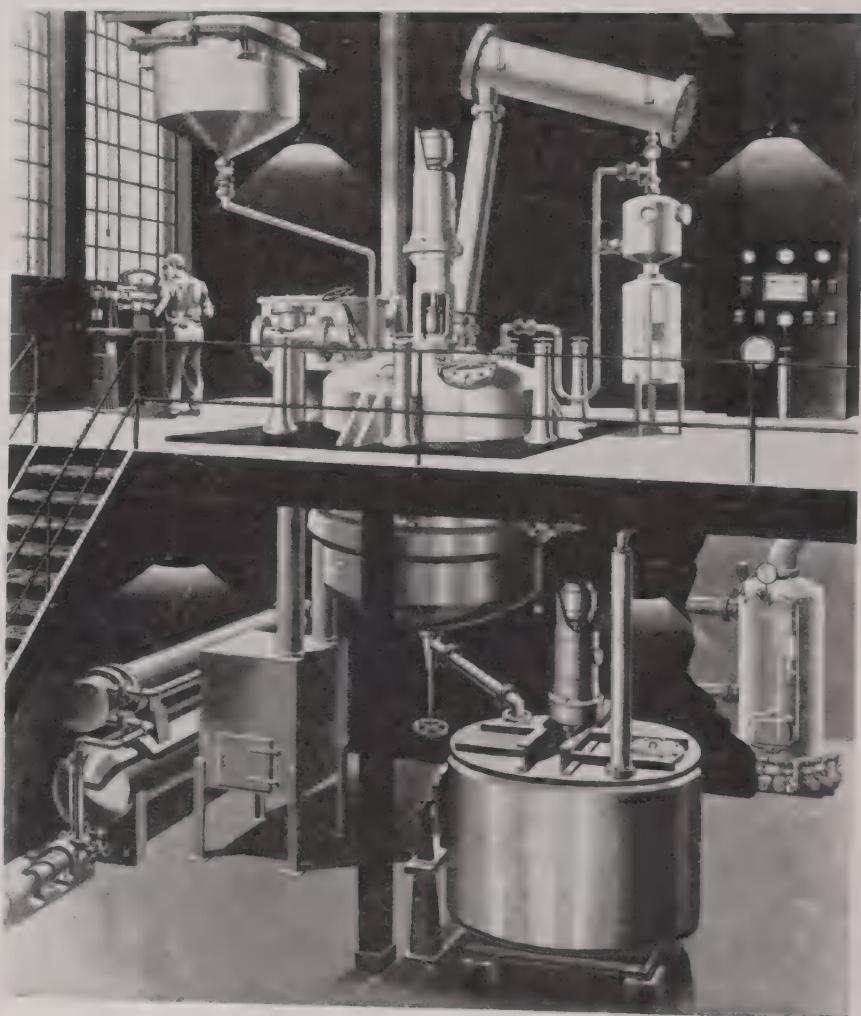
Fig. 57. Modern resin kettle and accessories (Courtesy *Blaw-Knox Construction Co.*).

The necessity for moving the kettle and of heating and cooling through the kettle surface limited the capacity to a maximum of about 350–400 gallons.

Modern production requirements, coupled with complications introduced by the use of such products as alkyd resins, have brought about great changes in cooking equipment. Recent installations have made use of closed, mechanically agitated kettles, of Type 316 or Type 347 stainless steel, equipped with jackets for Dowtherm heating or cooling (see page 785), and provided with accessory equipment which may include pumps or steam ejectors for producing vacuum, condensers for returning or taking off volatile products, fume scrubbers, and/or burners, and inert gas systems for stripping the batch or flooding the kettle headspace. Such systems (Fig. 57) are versatile and capable of handling drying oil products through a variety of processing operations, including varnish cooking, heat bodying, esterification and synthesizing reactions, and the dehydration of castor oil. Kettle capacities of 2000–3000 gallons are common, and the largest alkyd resin installations have kettles holding as much as 8000 gallons. Formerly, the usual practice after cooking was to add volatile thinners or solvents in the kettle, but modern installations utilize separate closed thinning tanks equipped with reflux condensers to prevent loss of material. In general, the more elaborate arrangements are designed primarily for alkyd resin manufacture and other esterification work, although closed mechanically agitated kettles with electric or Dowtherm heating are now generally preferred for ordinary varnish cooking.

In varnish cooking, the sequence of operations depends greatly upon the raw materials used. Fossil resins do not become compatible with drying oils at ordinary cooking temperatures of 500–600°F., but must be subjected to a preliminary "melting," "cracking," or "running," at 625–650°F., or even higher. Extensive heat degradation occurs, with a substantial loss of material, e.g., 20–30%. Other resins, e.g., recent natural resins, ester gum, or common phenolic resins, may be simply cooked with the oil. In the preparation of baking finishes with heat-reactive phenolics it is necessary to incorporate the resins only after cooking is substantially completed. Tung oil used in varnishes must be subjected to a short period of high-temperature treatment if the product is to be "gasproof." For the most thorough gasproofing tung oil must be treated separately, but some measure of gasproofing is often obtained by carrying the oil quickly to 550–600°F. in the kettle, and then rapidly cooling it. For this cooling, and also for cooling the batch quickly at the end of the cooking period—to stop reaction—the practice is often followed of "checking," or rapidly adding resins or a portion of cold oil. Some resins of limited oil compatibility are preferably cooked first with a little oil until a bead of the cooled product is clear, after which the remainder of the oil is worked in, in successive portions, with repeated heating and testing.

The end point in the cooking operation is determined by the viscosity of the batch, which is judged according to the "stringiness" of the cooled

or partially cooled material, or is actually determined (after dilution with a thinner) in a simple "bubble-tube" viscometer. If thinning is to be carried out in the kettle, the batch must then be cooled to 350–400°F. before the relatively volatile thinner can be added. Cooling is greatly simplified and better control of polymerization is obtained if separate thinning tanks with agitators and adequate condensers are provided, because with these it is not necessary to cool the hot material as much before it is dropped and mixed into the cold thinner.
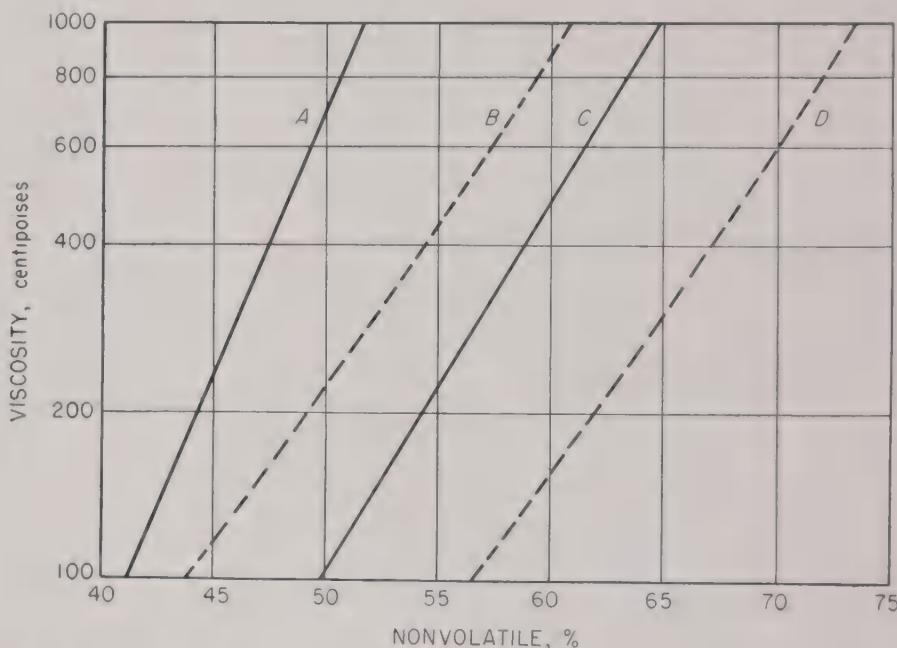
Fig. 58. Relation between content of nonvolatile material and viscosity in varnishes and alkyd resins after thinning with mineral spirits: (A) 52% oil-modified alkyd resin (alkyd ratio, 48)[116]; (B) 58% oil-modified alkyd resin (alkyd ratio, 42)[116]; (C) 15 gal. linseed oil-congo resin varnish, medium melt[138a]; (D) 15 gal. linseed oil–congo resin varnish, fine melt.[138a]

Varnishes or enamel vehicles are usually thinned to a viscosity at 77°F. of about 0.5–1.5 poises or A to F on the Gardner-Holdt scale, with the nonvolatile content of the thinned material varying between about 40 and 60% by weight. In the range with which the varnish maker is concerned there is very nearly a straight-line relationship (Fig. 58) between the content of nonvolatile component and the logarithm of the viscosity, with an increase of 4–5% in the former halving the viscosity.[116,138a] For a reasonably close control of the viscosity, therefore, the proportion of thinner incorporated is fairly critical. Dryers are usually added in soluble form during the thinning operation.

[138a] F. M. Damitz, J. A. Murphy, and J. J. Mattiello, in *Protective and Decorative Coatings*, Vol. III, J. J. Mattiello, ed., Wiley, New York, 1943, p. 221.

(b) Manufacture of Alkyd Resins

Whereas in ordinary varnishes the relative proportions of resins and oil are defined quite simply by the "oil length" (page 456), this nomenclature is not well adapted to alkyd resin products in which the resin is not preformed, but is produced in the kettle as polymerization proceeds. As has been mentioned previously (page 444), the corresponding composition of alkyd resins is customarily expressed in terms of the "alkyd ratio," or theoretical percentage of glyceryl phthalate in the product, assuming that three mols of phthalic anhydride combine with two mols of glycerol. Thus, long-oil alkyds have low alkyd ratios, *e.g.*, 25 to 35, whereas short-oil alkyds have high alkyd ratios, *e.g.*, 50 to 65.

The establishment of a given alkyd ratio does not exactly establish the relative proportions of glycerol (or other polyhydric alcohol) and phthalic anhydride (or other dibasic acid) in the formula, although, for reasonably complete over-all esterification, the ratio of phthalic anhydride to glycerol naturally becomes high in short-oil alkyds and low in long-oil alkyds. Detailed data on a variety of actual commercial formulas are not available; however, in the manufacture of a medium oil length product (with an alkyd ratio, for example, of about 40 to 50) it appears that it is usual to employ approximately one mol of phthalic anhydride per mol of glycerol. An alkyd resin modified with soybean fatty acids (average molecular weight, 280) and made to have an alkyd ratio of 46, might thus have as its raw materials the following: fatty acids, 44%; phthalic anhydride, 35%; glycerol (anhydrous basis), 21%. At a "Q" viscosity or *ca.* 4.35 poises (when diluted with 50% of mineral spirits), an acid value of about 10–12 and a hydroxyl number of 80–85 might be expected. Pentaerythritol is said to esterify as readily as glycerol in alkyd resin manufacture, since it contains only primary hydroxyl groups. However, all of the hydroxyl groups of sorbitol are not available for esterification, and allowance must be made for this fact when it is substituted for glycerol or pentaerythritol in a formula.

When free fatty acids are used as the modifier for alkyds, the reaction is quite straightforward. All ingredients are simply reacted together in an inert atmosphere at 425–475°F. for 3–5 hours, or until the desired viscosity and acid value are reached; there are optimum combinations of the two for any given formulation, and in general, the acidity becomes lower as the oil length increases. Often, the product is only partially modified with fatty acids and oil is added later during the reaction. At the proper point, the reaction is checked by dropping the hot batch into a carbon dioxide blanketed thinning tank containing cold solvent. The final viscosities desired in the thinned products and the amounts of thinner required are not very different from those mentioned above for ordinary varnishes.

The selection of the thinner depends to a considerable degree upon the oil length of the alkyd. Products containing 50% or more oil are said to be quite freely soluble in aliphatic petroleum thinners, whereas products of shorter oil length require stronger solvents.

If an oil (rather than fatty acids) is to be used exclusively for modification, reaction of the relatively inert oil with phthalic anhydride and free glycerol will tend to cause the latter two components to polymerize without benefit of oil modification, with the formation of insoluble material. Hence, as a preliminary step, it is necessary to react the oil and glycerol, to form mono- and diglycerides,[139] after which phthalic anhydride may be added and reaction continued in the usual manner. The preliminary glycerolysis of the oil is conducted at the same temperature as the second stage of the reaction (425–475°F.), in the presence of calcium, sodium, or lead soaps as a catalyst, and is usually completed within about an hour or two after the batch reaches operating temperature. It is usually judged to be at an end when the reaction product becomes freely miscible with alcohol.

Alkyds prepared by the monoglyceride method are said to have somewhat different properties from comparable alkyds made with fatty acids, *i.e.*, they are softer and slower drying and more easily soluble; also, the properties of the product may be modified by withholding a portion of the fatty acids or a portion of the phthalic anhydride during the early part of the reaction. The difference between alkyds made by the fatty acid method and by the monoglyceride method has been attributed to specific differences in the molecular structure of the two products, occasioned by differences in the reactivity of phthalic anhydride and of fatty acids with the α- and β-hydroxyl groups of glycerol.[121] However, it is difficult to reconcile the formation of more or less specific molecular structures with the known tendency for ester interchange to occur under the conditions of reaction. Actually, the reaction product of fatty acids with an excess of glycerol does not consist exclusively of mono- and/or diglycerides, but is an equilibrium mixture of these compounds with triglycerides and free glycerol, in which fatty acid radicals are esterified in a random manner with the available hydroxyl groups (see page 836). The esterification product of two mols of fatty acids with one mol of glycerol, for example, does not consist substantially of diglycerides, as has sometimes been assumed, but at equilibrium has the following composition (mol percentages): triglycerides, 29.6; diglycerides, 44.2; monoglycerides, 22.2; free glycerol, 3.7.

Although the initial reaction in the monoglyceride method must be

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[139] K. Ott, H. Bernard, and F. Frick (to E. I. du Pont de Nemours & Co.). U. S Pat. 2,044,747 (1936).

regarded as essentially an aid to subsequent ester interchange, rather than a step in which molecular structure is rigidly fixed, it appears reasonable, nevertheless, to expect that this method will produce a less homogeneous product than the fatty acid method.

The characteristics of the reaction depend somewhat upon the alkyd ratio of the product. Since phthalic anhydride reacts with glycerol more readily than fatty acids, and since the α-hydroxyl groups of glycerol are more reactive than the inner or β- group, the tendency is to form linear polymers, as depicted in Part A of Figure 59. With a relatively low ratio
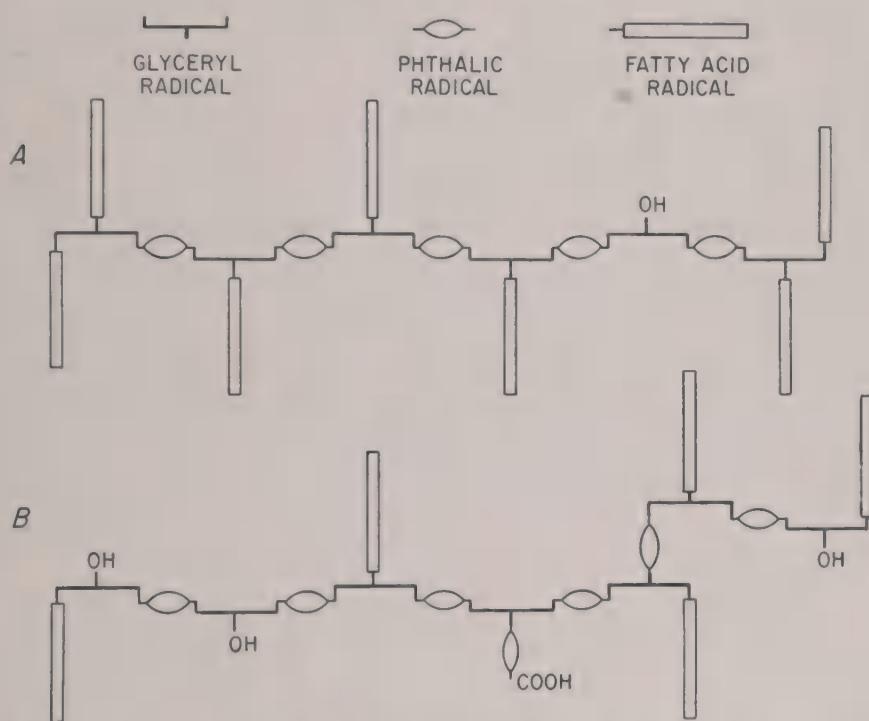
Fig. 59. Schematic and simplified representation of molecular structure in alkyd resins of: (A) long-oil type, and (B) short-oil type.

of phthalic anhydride to glycerol, and a high ratio of fatty acids to either (as in long-oil products), there is a tendency for the linear polymer chains to grow to a certain average length, and then terminate, as indicated in Figure 59 (Part A). The final concentration of unreacted hydroxyl groups, as well as free carboxyl groups, tends to be low. On the other hand, in short-oil alkyds, as illustrated schematically in Part B, a comparable degree of polymerization will leave both hydroxyl and carboxyl groups free and reactive. As the presence of these permits cross bridging between adjacent polymer units, continued reaction will lead to gelation. Stopping

of the reaction short of gelation will yield a product higher in acidity than a long-oil alkyd, and one considerably higher in hydroxyl value. Although only α-esterification of phthalic anhydride is envisioned in the ideal reaction, there is actually, of course, some β-esterification, to produce chain branching, as illustrated in Part B, Figure 59. In straight alkyd resins, if not those of the oil-modified type, some intraesterification and anhydride formation also occurs.[119]   In any case, a reasonably low acidity can be attained only by providing a substantial excess of hydroxyl groups.
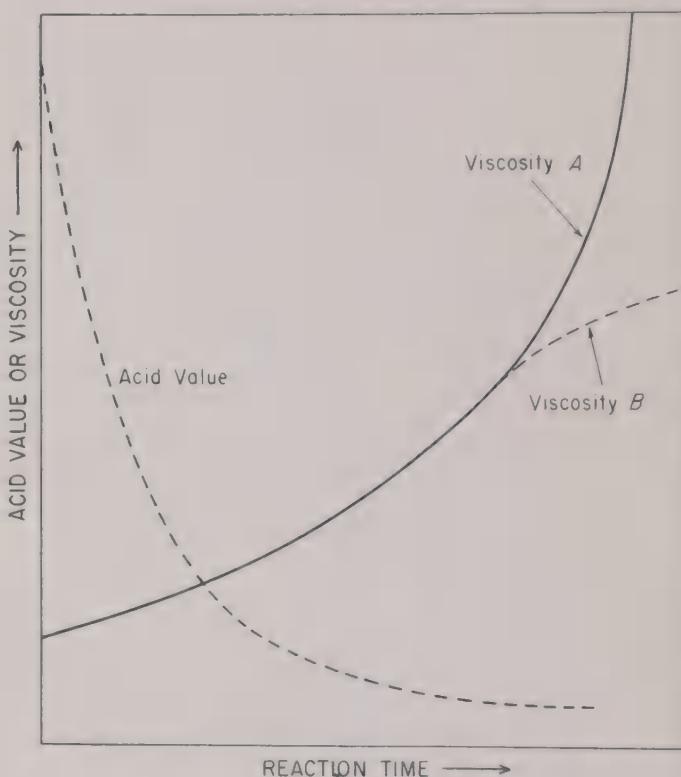
Fig. 60.   Idealized representation in alkyd resin manufacture of fall in acid value and increase in viscosity of: (A) short-oil type, and (B) long-oil type, according to reaction time.

So long as polymerization is confined to the formation of linear polymers, and so long as functionality does not decrease with the advance of polymerization, alkyd resins tend to body like drying oils (page 898), i.e., there is substantially a linear increase in the logarithm of the viscosity (or solution viscosity) with increase in the reaction time. With alkyds of the short-oil type, the rate of viscosity increase eventually quickens and the viscosity rises rapidly toward the point of gelation, yielding a curve of viscosity vs. time similar to curve A of Figure 60. Presumably, the point of upward deviation (from logarithmic relationship) marks

the begininng of cross bridging.[116] In the case of long-oil alkyds, deviation toward the end of the reaction is in the opposite direction, with the rate of viscosity increase falling off as termination of linear chains occurs (curve B). Alkyds of great length may even reach a nearly constant "terminal viscosity" (curve B). As reaction proceeds, the acid value falls off at a steadily decreasing rate, often in such a manner as to maintain at first a direct relationship between the acid value and the reciprocal of the viscosity.

(c) "In Situ" Preparation of Other Resins

Varnishes other than those of the alkyd resin type are sometimes prepared by the "in situ" method, i.e., by forming the resin in the oil during the cooking process. Rosin may be reacted with glycerol, pentaerythritol, or another polyhydric alcohol and either a drying oil or drying oil fatty acids. The complete reaction requires several hours in a closed kettle with agitator, at a temperature of 550–575°F.

2. MIXING AND GRINDING[139a]

The most critical and most expensive mechanical operation in paint and varnish manufacture is the grinding or dispersion of solid material in pigmented finishes. In the grinding of pigments the sole object is to break up agglomerates of solid particles and cause all portions of each particle to become uniformly wetted by the liquid vehicle. There is virtually no reduction in particle size, inasmuch as all pigments are supplied in a very finely divided form. Although simple in principle, the operation is often relatively difficult in practice; as explained elsewhere, the ease of dispersion is influenced very markedly by the surface activity of the pigments, and more particularly, by that of the vehicle.

Wherever possible, it is preferred to grind a relatively concentrated paste, which can subsequently be thinned in making up the finished product. In some cases, however, it is necessary to grind a thinned material containing a volatile solvent. Such a product, of course, requires a closed mill.

The most common open mills are *stone mills*, in which the material is ground between a flat horizontal rotating stone opposing a similar fixed member, and *roller mills*, consisting of a series of superimposed steel rollers rotating at different speeds, between which the oil–pigment mixture is passed. The more popular closed mills include ordinary *pebble* or *ball mills*, and a special device, the *Bramley mill*, which consists of a

[139a] For a recent description of mechanical operations and equipment in a modern paint factory, see W. H. Shearon, Jr., R. L. Liston, and W. G. Duhig, *Ind. Eng. Chem.*, *41*, 1088–1097 (1949).

horizontal drum, inside of which there is a rotating assembly of flexible blades engaging a similar assembly attached to the drum or shell. Grinding is effected by the rubbing and wiping action of the one set of blades upon the other.

Except for certain siliceous extenders, paint pigments are usually soft and nonabrasive; hence the wear on mills is relatively low.

For rough mixing of pastes prior to grinding, various small, highly powered mixers are used, including "lead mixers" with heavy vertical stirrers, edge runners or "putty chasers," and mixers with horizontal stirrers, of the Banbury type.

The operations of mixing and grinding are often complicated by the necessity of handling many different colors without contaminating one product with another; hence the capacity of individual units tends to be small. The capacity of mixers and batch mills is often not greater than 100–150 gallons.

3. Other Mechanical Operations[139a]

The blending and mixing of ground pigments, oils, varnishes, and thinners to produce the finished paint or enamel is usually carried out in stationary tanks equipped with paddle or turbine-type agitators, although portable tanks may be used for small batches. Batches are adjusted to a standard color in these tanks, by the addition of small amounts of shading or tinting pastes. Before the product is packaged it is run through a vibrating screen, for the removal of shreds of polymerized "skins." Enamels for very high grade finishes are also subjected to centrifugal "clarification" at this point. Clear varnishes and other vehicles are clarified centrifugally, or, when extreme freedom from solid particles is required, they are filtered through plate-and-frame presses. Filling of the material into cans, labeling, etc., are carried out with automatic machinery.

G. Relation of the Oleoresinous Vehicle to Various Properties in Paints and Related Products

1. Keeping Quality in the Package

The ability to withstand long periods of storage in the package is a prime requisite in paint products, since months or even years may elapse between manufacture and use of these materials.

Since all paint pigments are heavier than the vehicles in which they are suspended, there is some tendency of pigments to settle to the bottom of the stored cans. Under some conditions they may settle out in the form of a hard cake, which will be difficult to mix back into the vehicle. Such a caking tendency is of course highly undesirable.

The causes and control of settling and caking in paints have been discussed by Croll,[140] Werthan, Wien, and Fatzinger,[141] Gamble,[142] McMillen and Glaser,[143] and others. Theoretically, settling can be minimized by decreasing the effective particle size of the pigment or increasing the viscosity or plasticity of the pigment–vehicle system, so that the gravitational force inclining the pigments to settle will be small relative to the resistance to settling offered by the vehicle. Actually, however, attempts to control settling in this manner are not always successful, since they tend merely to slow the settling process, without necessarily having any effect upon the condition finally attained by the product after long storage. This is particularly true if a high degree of pigment dispersion is depended upon to inhibit settling. Highly dispersed pigments settle slowly, but are inclined to form hard cakes if allowed to settle for a sufficient time.

Another means of combating the undesirable effects of settling is through control of the character of the settled pigment structure. Settling is not necessarily troublesome *per se*, but is undesirable because of its relation to hard caking. If the settled pigments form a soft cake, which is readily reincorporated with the oil, the readiness with which the cake is formed may be more or less immaterial. The consistency of settled paint pigments is closely related to their degree of flocculation. If the pigment particles are highly wetted by the vehicle, or in other words, if they have a high affinity for the vehicle and a correspondingly low affinity for one another, they will tend to settle as discrete particles, with close packing and the formation of a hard cake. On the other hand, if they have a relatively low affinity for the vehicle and a strong mutual affinity, so that they tend to clump together in irregular masses, the settled pigment structure will be skeletal, enclosing much of the liquid phase, and soft in consistency.

Pigment wetting and flocculation may be controlled to some degree by suitable choice of the oils used in the vehicle. Thus, heat-bodied oils wet pigments more readily than raw oils, and the degree of wetting tends to increase with the viscosity of the oil. Blown oils have even stronger pigment-wetting properties than bodied oils.

Since flocculation and dispersion in paint products are surface phenomena, it is to be expected that they may be influenced by the presence in the vehicle of small concentrations of substances possessing surface activity. The substances most commonly added to paints to inhibit hard settling are water (usually to the amount of less than 1%, in the form of

[140] P. R. Croll, *Ind. Eng. Chem.*, 20, 734–735 (1928).
[141] S. Werthan, R. H. Wien, and E. A. Fatzinger, *Ind. Eng. Chem.*, 25, 1288–1292 (1933).
[142] D. L. Gamble, *Ind. Eng. Chem.*, 28, 1204–1210 (1936).
[143] E. L. McMillen and D. W. Glaser, *J. Applied Phys.*, 9, 502–507 (1938).

a weak soap solution), and metallic soaps, such as aluminum stearate. It is to some extent uncertain how much of the action of these materials is due to surface activity, or modification of the wetting characteristics of the vehicle, and how much is due to the formation of a gel structure in the vehicle. In the case of the metallic soaps, gel formation may be the predominant factor, but water is effective in smaller quantities than are required for strengthening of the vehicle structure through emulsion; hence it probably functions primarily as a flocculating agent.

The defect in paint products known as afterthickening, or if very pronounced, as "livering," involves a thickening of the material in the package. Livering is the result of gel formation in the vehicle, and hence is not related to pigment dispersion, although it is influenced by the chemical nature of the pigment. It occurs most pronouncedly in products made with vehicles of high acidity and reactive pigments. It appears probable that it results largely from gel formation by metallic soaps. However, it has been suggested that highly polymerized oils may be involved in the process,[144] and that gelling occurs after the acidic components of the vehicle have become neutralized, and no longer able to exert a peptizing action.

Livering may be controlled by avoiding the use of highly acid oils, especially with pigments such as zinc oxide, which readily form soaps with free fatty acids. In the case of bodied oils, the method of bodying has a pronounced influence upon livering tendencies.[82]   Oils bodied under vacuum form products with less tendency to liver than ordinary oils bodied with access to the air.

Granulation in a paint is usually the result of the deposition of small masses of metallic soaps from the vehicle, and is inclined to occur only with the combination of high-acid oils and reactive pigments. Quick-drying varnishes or other products which are inclined to gel with limited oxidation will occasionally form a polymerized film over the surface of the can. This defect is known as "skinning." It may be inhibited by the addition of "antiskinning" agents.

2. Ease of Application

Paints, varnishes, and enamels are applied by brushing, spraying, or dipping, as may be the easiest and most convenient method. The manufacture of products which are thin enough to be applied readily by one of these methods, and yet which have sufficient body to "stay put" and form a uniform coating is not always easy, and requires that careful consideration be given to the physical structure of the material.

A protective or decorative coating applied to an inclined surface must

[144] Chicago Paint & Varnish Production Club, *Natl. Paint, Varnish Lacquer Assoc. Circ.* No. 471, 289–294 (1934); *Am. Paint J., 18,* No. 53D, 14–16; *Paint Oil Chem. Rev., 96,* No. 22, 58–62 (1934).

not flow to an appreciable extent during the drying period if it is to form a uniform film of good appearance and maximum protective properties. Films of varnishes or fast-drying enamels may have sufficient viscosity to retain their form during the brief period elapsing between application and the beginnings of gelation. In the case of paints and other slowly drying products, a certain degree of plasticity is essential to prevent "running" or "sagging" of the films. On the other hand, it is not desirable for a paint to be completely resistant to flow after application, particularly if it is to be applied by brushing. The ability of the paint to flow slightly permits "leveling," or the elimination of brush marks or other film irregularities by surface tension forces.

The manner in which the pigment is dispersed in the vehicle is of extreme importance in determining the body characteristics of the paint. Highly flocculated pigment—oil systems tend to be stiff and plastic, whereas dispersed systems are thin and lacking in plasticity. As mentioned previously, flocculation may be greatly influenced by the presence of surface-active substances developed in the oil by heat bodying or blowing, by the reaction of basic pigments with free fatty acids to form soaps, or by the addition of water, metallic stearates, etc. The effect of surface-active substances in producing defflocculation and consequent loss of plasticity in a pigment—oil system is dramatically illustrated in the experiment cited by Green,[145] wherein the addition of one or two drops of heat-bodied poppyseed oil suffices to convert a stiff mixture of zinc oxide and mineral oil to a soft and fluid mass. Fischer and Jerome[146] have published the results of a large number of experiments involving the use of synthetic wetting agents to increase or decrease the flocculation of pigments in various vehicles. It is to be noted that the degree of flocculation or dispersion to be attained in a specific system is determined by the characteristics of the pigment as well as the vehicle, and that different pigments respond differently to surface-active agents, according to whether they are naturally hydrophilic or lipophilic. Thus, for example, ultramarine is considered a hydrophilic pigment, whereas carbon black is lipophilic.[146] The former is consequently relatively responsive to defflocculating agents, whereas the latter responds more easily to flocculating agents. For photomicrographs illustrating typical flocculated and dispersed pigment—oil systems the reader is referred to such publications as those of Green,[145] Fischer and Jerome,[146] and Troutman.[147]

The plastic behavior of paints, printing inks, etc. is much influenced by the tendency of these products to behave thixotropically. Thixotropy

[145] H. Green, *Ind. Eng. Chem.*, 15, 122–126 (1923).
[146] E. K. Fischer and C. W. Jerome, *Ind. Eng. Chem.*, 35, 336–343 (1943).
[147] R. E. Troutman, in *Protective and Decorative Coatings*. Vol. III, J. J. Mattiello, ed., Wiley, New York, 1943, pp. 333–385.

is exhibited by all pigmented paint products,[148-150] and even to some extent by oils alone.[151] Speaking from the standpoint of the practical paint technologist, thixotropy may be defined as the tendency of viscous or plastic materials to become less viscous or to exhibit lower yield values after being stirred, brushed, or otherwise subjected to internal shear. It is a reversible phenomenon; the material regains its original viscosity or plasticity when allowed to remain undisturbed again for some time. Thixotropy may be so pronounced as to be evident to casual observation. It can be detected and evaluated in the laboratory by the technique described by Green and co-workers,[149,150] which involves successive measurements of apparent viscosity at increasing and decreasing rates of shear with a viscometer of the rotational type.

Sometimes the term "false body" is applied to the consistency possessed by paints with marked thixotropic properties. According to Gamble,[142] false body cannot be clearly differentiated from thixotropic body, but refers in general to body which is quickly regained after disturbance of the material ceases. The recovery of thixotropic body is relatively slow. In the older literature, the term "false body" is often used with a somewhat different meaning. Thus, for example, Werthan et al.[141] refer to false body as the type of body which may be irreversibly lost as a result of working of the material, for example, through the breakdown of an emulsion.

Thixotropy in some paints may be due in part to the existence of a certain degree of gel structure, but is also undoubtedly associated with the phenomenon of flocculation. In other words, a paint which has had its consistency reduced by stirring, brushing, etc., may be considered temporarily deflocculated, the recovery of body after agitation has ceased being coincident with the re-establishment of flocculative forces between the pigment particles. The thixotropic characteristics of paints and related materials may therefore be modified by the methods described above for inducing or inhibiting flocculation. Kewish and Wilcock[152] have observed a minimum pigment concentration for the appearance of marked thixotropy, which is in the neighborhood of 30% of pigments by volume in the system.

In general, some degree of thixotropy is desirable in paints. Thus a brushing paint with optimum thixotropic characteristics may thin under the influence of the brush, so as to spread readily, retain its thin consistency long enough for good leveling to take place, and then recover its

[148] J. Pryce-Jones, *J. Oil Colour Chem. Assoc.*, *17*, 305–375 (1934); *19*, 293–337 (1936).

[149] H. Green, *Ind. Eng. Chem., Anal. Ed.*, *14*, 576–585 (1942).

[150] H. Green and R. N. Weltmann, *Ind. Eng. Chem., Anal. Ed.*, *15*, 201–206 (1943).

[151] R. N. Weltmann, *Ind. Eng. Chem., Anal. Ed.*, *15*, 424–429 (1943).

[152] R. W. Kewish and D. F. Wilcock, *Ind. Eng. Chem.*, *31*, 76–83 (1939).

original thick consistency in time to prevent running or sagging.[153] Thixotropy is a particularly useful property in printing inks. These materials are applied in very thin films, and hence must be pigmented as intensely as possible. A thixotropic ink, which thins markedly during application, may contain a larger proportion of pigment without being excessively thick than a nonthixotropic product.

The degree to which the pigments are wetted by the vehicle has a large influence on the tendency of the vehicle in priming paints to be absorbed by wood surfaces. If the pigments and the vehicle have a high mutual affinity, the vehicle will be relatively little inclined to be drawn out of the undried film into the wood. Deep penetration of the wood by the vehicle was formerly considered desirable, but it is now known that such penetration is merely wasteful.[132] Vehicle penetration must be inhibited by the use of strongly wetting oils, etc., in the primers used for two-coat house painting, in order to permit the application of a thick priming coat.

Since the factors of pigment settling, ease of spreading, leveling, running, penetration, etc., are all closely related to the matter of pigment flocculation, it will be seen that in general it is not possible to modify the vehicle for the purpose of influencing one of these factors without some effect upon each of the others. The very high development of one desirable characteristic may preclude the proper development of other characteristics of equal desirability and importance, or may have an unfavorable effect on the chemical properties of the product. The practical formulation of paint materials of good physical characteristics, therefore, involves a series of compromises between mutually exclusive properties, in order to obtain products with the best all-around characteristics for the purpose for which they are intended. A schematic representation of the qualitative relationships obtaining among the various factors discussed above, is presented in Table 96.

The method by which printing inks are applied is fundamentally different from the methods employed for the application of paints, varnishes, etc. This difference introduces certain requirements in the way of consistency in these materials. Inks are applied by bringing the ink-coated printing plate in contact with the paper or other material, to cause the ink to adhere to the latter surface, and then separating the surfaces of plate and paper. Unless the paper is so absorbent as practically to remove all ink from the plate, there is in the process of separation a rupture of the ink film somewhere between the two solid surfaces. The resistance offered by the ink to this rupture is referred to as its tack.

As indicated previously, the tack of printing inks is of great importance, particularly in the case of process inks for color printing, since the successful application of successive colors requires that each color be more

[153] E. L. McMillen, *Ind. Eng. Chem.*, *23*, 676–679 (1931).

tacky than the color applied over it, in order that film rupture may occur in the top, rather than in the bottom film. Green[138] has reported the relative tacks of a variety of printing inks, as measured by a specially designed "tackmeter," and has discussed the theory of this property in some detail.

The speed with which a paint dries often has an important bearing upon its ease of application. The drying time requirements for different prod-

TABLE 96

RELATION OF PIGMENT-VEHICLE REACTIVITY TO VARIOUS PHYSICAL PROPERTIES
OF PAINTS AND RELATED PRODUCTS

A.   Physical reaction between pigments and vehicle

Wetting of pigments by vehicle	Nonwetting of pigments by vehicle
Dispersion of pigments	Flocculation of pigments
Thin body	Thick body
Hard caking	Soft caking
Nonthixotropic	Thixotropic
Hard spreading	Easy spreading
Good leveling	Poor leveling
Sagging	Nonsagging
Limited penetration on wood surfaces	Deep penetration on wood surfaces
Lipophilic pigments	Hydrophilic pigments
Bodied oils—blown oils	Raw oils—overbodied oils
No water in vehicle	Water in vehicle
Wetting agent in vehicle	Nonwetting agent in vehicle

B. Chemical reaction between pigments and vehicle

Nonreactivity between pigment and vehicle	Reactivity between pigment and vehicle
No gel structure in vehicle	Gel structure in vehicle
Thin body	Thick body
Nonthixotropic	Thixotropic
Settling	Nonsettling
Good leveling	Poor leveling
Hard spreading	Easy spreading
Sagging	Nonsagging
Not inclined to liver	Inclined to liver
Nonreactive pigments	Reactive pigments
Low acidity in vehicle	High acidity in vehicle
	(Added metallic soaps)

ucts vary a great deal. House paints and other exterior finishes are generally considered satisfactory if they will dry reasonably well overnight, under ordinary atmospheric conditions. At an opposite extreme are products used in connection with assembly line production, such as automotive finishes, which under the accelerative influence of heat, are in most cases dried in much less than an hour.

As mentioned previously, the drying rate of an oil is determined pri-

marily by the number and type of its unsaturated linkages. In the case of oils containing no conjugated double bonds, the drying rate of the oil is in general shorter, the higher the iodine value. However, the type of glycerides in the oil, as well as their over-all degree of unsaturation, have some influence on the drying rate. Fish oils, for example, are generally more highly unsaturated than linseed oil, but they have a high content of completely saturated fatty acids, and hence are relatively slow in forming hard films. Conjugated acid oils dry much more rapidly than equally unsaturated oils which do not contain conjugated double bonds.

Since drying is to a large extent a phenomenon of oxidation, the drying time of an oil is shortened by the presence of pro-oxidants, and lengthened by the presence of antioxidants. The metallic dryers commonly used in paints and varnishes serve as pro-oxidants. The natural antioxidants of drying oils are oxidized and destroyed during the operations of blowing or heat bodying.

The drying time of an oil may be greatly shortened by partially polymerizing (heat bodying or blowing) it before it is applied and by incorporating with it resins which are more reactive with respect to polymerization than is the oil. These methods of shortening the drying time are employed in the manufacture of varnishes and quick-drying enamels.

3. Appearance of the Applied Films

In most applications, paints and other coating materials are required to fulfill a decorative as well as a protective role; hence the appearance of the applied films is a matter of considerable consequence. While the color, hiding power, gloss, color retention, etc., of such products are largely determined by the characteristics or proportions of the pigments, these properties are also affected to some extent by the vehicle.

The hiding power of a paint, or the ability of the paint to obscure the surface over which it is applied, is principally a function of the pigments used. However, Lightbody and Dawson[154] have reported that differences of up to 20% in the hiding power of enamels can be produced by the use of different vehicles of the same color and refractive index. In the absence of a better explanation, they attributed these differences to variable deflocculation of the pigments, although there was no experimental evidence of this. Dark-colored vehicles tend to increase hiding power, as compared with light-colored vehicles.[155]

The color of the lighter paints and enamels is considerably affected by the color of the vehicle; only light-colored oils are used in the manufacture

[154] A. Lightbody and D. H. Dawson, *Ind. Eng. Chem., 34,* 1452–1456 (1942).
[155] R. A. Morrison, *Official Digest Federation Paint & Varnish Production Clubs,* 4, No. 112, 745–749 (1932).

of enamels of light, bright shades. Color retention is very decidedly influenced by the nature of the vehicle. Yellowing of white paints and enamels is dependent upon the unsaturation of the oil (see previous discussion of deterioration in paint films, page 423), being little evident in soybean oil, dehydrated castor oil, or other oils containing inconsiderable amounts of fatty acids with more than two double bonds. Colored paints of the gloss or semigloss types retain their color and appearance much better when the vehicle is fortified with resins or varnishes. A slight chalking tendency, which may be beneficial in the case of a flat white paint because of its self-cleaning action, is very detrimental to the appearance of a brightly colored, glossy finish, and may render the latter inadequate from the decorative standpoint long before deterioration has progressed to the point of failure in protection.

Gloss in a paint or enamel film is principally determined by the ratio of vehicle to pigments and the fineness of the pigments, but it may also be affected by the presence of certain substances in the vehicle. The presence of small amounts of water and of metallic soaps, such as aluminum, zinc, or calcium stearates, is unfavorable to the production of high gloss. The effect of these substances on gloss restricts their use as bodying or flocculating agents in some products. In certain cases the metallic soaps may be added specifically for their flatting action.

4. Serviceability of the Applied Films

Failures of protective coating films may be divided into three categories: (a) failure of the film by simple wear or erosion; (b) failure in the structure of the film, resulting in cracking, checking, chalking, etc.; and (c) failure of the film to adhere, which may or may not be preceded or accompanied by structural failure.

Film failure due to wear or abrasion is chiefly confined to interior finishes, and others which must be periodically washed or cleaned. Such finishes are generally of the varnish or enamel type. The determining factor in the durability of a film under abrasive conditions appears to be its hardness, which is in turn related to the type of resin employed in the vehicle. Varnishes and enamels employing the synthetic resins in their composition are outstanding in abrasion resistance. In general, the more highly unsaturated is a drying oil, the harder are its films. Pigment flocculation in a paint or enamel is considered detrimental to the hardness of the film. In exterior architectural finishes, film failure through simple wearing away of the film is rare, although a similar effect is produced by pronounced chalking.

The most common type of film failure is structural, and occurs through gradual alteration of the physical properties of the film as a result of

oxidation and continued polymerization. The prime cause of this type of failure appears to be a loss of elasticity or of toughness in the film, resulting in eventual cracking or checking, through inability of the film to accommodate itself to externally or internally generated stresses. The relation between loss of elasticity and film failure has been the subject of investigations by Hunt and Lansing,[156] and Blom and Krumbhaar.[157]

Extreme hardness and resistance to abrasion in a protective coating may be considered more or less incompatible with the elasticity and resistance to embrittlement which is required for long life under exposure to sunlight and other weathering influences. Varnishes and enamels are much more inclined to crack or check with age than ordinary oil paints, and their resistance to this type of failure is in general in direct proportion to their oil length and the elasticity of the films. However, there are important exceptions to this generalization among products made with some of the synthetic resins. Tendency toward the type of failure known as "chalking," if not excessive is considered desirable in white house paints. Chalking is a surface type of disintegration, in which the surface of the paint film becomes powdery and gradually erodes away, without the development of structural faults deep within the film. A paint which chalks uniformly presents a continually clean, attractive surface during its lifetime, and after erosion has occurred to the point of exposing the painted surface, it offers the best possible foundation for repainting. The chalking tendencies of paints are dependent upon the pigments rather than the vehicle, however, being particularly enhanced by the inclusion of titanium dioxide in the formula.

Cracking of paint films is often preceded or accompanied by detachment of portions of the film from the underlying surface. Loss of adhesion, when accompanied by cracking, may be considered a result of the embrittlement caused by too advanced polymerization or oxidation, and hence related to the type of deterioration referred to above. Under the proper conditions, however, there may be failure of the film through lack of adhesion without pronounced deterioration of the film itself. Adhesion failure of the latter type may be the result of painting over greasy, rusty, moist, or excessively smooth surfaces. More often, however, it is caused by the collection of moisture under the paint film after the latter is applied.

In connection with the problem of moisture failure, it is to be noted that all films of paints, varnishes, or enamels are to some degree permeable to moisture. This permeability is greatest in ordinary oil paints, is less in coatings of the varnish or enamel type, and is very low in some of the varnishes prepared from the phenolic and other synthetic resins. With

[156] J. K. Hunt and W. D. Lansing, *Ind. Eng. Chem.*, 27, 26–29 (1935).
[157] A. V. Blom and W. Krumbhaar, *J. Oil Colour Chem. Assoc.*, 21, 338–354 (1938).

respect to the function of the coating material, a sharp distinction must be made between metals and other nonporous substances, and wood or similar materials which are permeable to moisture, and a further distinction must be made between wood members which are completely sealed by the coating material, and others which are coated on one side only, such as the sidings of frame dwellings. If the material painted is impervious to moisture, or if it is sealed on all sides by the paint, a maximum degree of waterproofness is desirable in the vehicle. But if it is sealed on but one side, it may be desirable for the paint film to be capable of transmitting moisture rather freely, as otherwise water may be driven through the wood from the unpainted side; if it is then unable to escape, it will collect between the paint film and the wood surface, causing the two to become nonadherent.

Although ordinary house paints are much more permeable to moisture than varnishes or enamels, they may exhibit moisture failure under adverse conditions. This type of failure has become much more prevalent since insulation of the walls of houses has become a common practice. If the insulating material is placed directly back of the siding, without an intervening air space, much of the temperature gradient from the inside of the house to the atmosphere will be in the siding, and moisture from the warm air within the building will tend to condense on the unpainted interior siding surface.

Metal surfaces are usually painted to avoid rusting; hence the water resistance of metal paints is important. However, in general, reliance is placed on a preliminary rust-inhibitive treatment, such as the Bonderizing process, or the use of rust-inhibitive pigments, rather than special vehicle formulations, to minimize rusting on painted metal surfaces. Moisture penetration of woods leads to warping and swelling, hence much attention is given to obtaining maximum waterproofness in spar varnishes or other coating materials for nonarchitectural wooden surfaces. The conjugated acid oils, and particularly tung oil, are outstandingly superior to ordinary drying oils for the manufacture of highly water-resistant varnishes. Among the products which are the most desirable in this respect are varnishes compounded from tung oil and the phenolic resins. For extreme water resistance, as required for example in interior coatings for tin cans, phenolic resin spirit varnishes, or very short tung oil varnishes of the baking variety are used.

MISCELLANEOUS OIL AND FAT PRODUCTS

In addition to the materials included in the major classes of oil and fat products, and described in the preceding chapters, there are a number of others of considerable industrial importance. In some cases these consist either wholly or substantially of fats or their derivatives; in others the fat or oil is an essential ingredient.

In general, the manufacture of these miscellaneous or specialty products is not standardized to nearly the same degree as that of the more widely used fatty products. Often their preparation is more of an art than a science, and the method of manufacture and the materials used vary widely from one manufacturer to another. Because of this, and also because of the great diversity of minor uses for fats and oils, it is hardly possible to review this field as comprehensively as those previously covered. However, an attempt will be made to indicate the nature and composition of the more important minor products.

In a considerable number of minor or specialty uses a fatty oil is employed because of its ability to dry or polymerize. In many applications where polymerization does not enter, the fatty oils compete to some extent with mineral oils. Since the latter are stable toward oxidation and also relatively cheap, they are generally preferred except where the distinctive properties of the fatty oils or fatty acids confer upon these materials particular advantages.

A. Drying Oil Products

1. Linoleum

The manufacture of linoleum is a relatively old industry. According to O'Hare,[1] the first linoleum factory was built in England in 1864, and by 1874, linoleum was being made in the United States. Over the course of years, empirical processing methods developed, and until rather recently treatment of the constituent oils has been traditional and largely unscientific, although high production requirements for a material with intricate inlaid designs has led to extremely ingenious and altogether revolutionary improvements in the machinery for linoleum manufacture.

[1] G. A. O'Hare, *J. Am. Oil Chem. Soc.*, *25*, 105–107 (1948).

The essential material for the manufacture of linoleum is a specially prepared, highly oxidized and polymerized drying oil which has been compounded with rosin, and usually other natural or artificial resins, to yield a stable, resilient, yet thermosetting product known to the industry as "cement." The cement is mixed with ground cork or wood and pigments or extenders and pressed onto a backing of burlap or other coarse fabric. In so-called inlaid linoleum, the design is made up of separate blocks or other figures of cement, which are pigmented with different colors. This method of manufacture causes the design to extend some distance into the linoleum, so that it is not readily worn away. Linoleum is flexible and resilient, relatively nonconducting to heat, and very durable. True linoleums are to be distinguished from the much cheaper and less durable felt-base floor coverings, which are made by impregnating a feltlike material with bitumen, and applying and baking onto the upper surface a thick coating of enamel.

The manufacture of felt-base floor coverings has been described briefly by O'Hare.[1a] In 1948 the United States production of linoleum and felt-base floor coverings amounted to 75 and 280 million square yards, respectively.[1a]

The first step in the manufacture of linoleum is the oxidation and polymerization of a suitable drying oil or mixture of drying oils until a relatively dry and nontacky solid is produced. Linseed oil is the most suitable raw material, although soybean and fish oils are also used to some extent. Tung oil or other conjugated acid oils tend to polymerize without extensive oxidation, and hence are unsuitable. The process is emphatically one of oxidation polymerization, rather than heat polymerization; it is essential for the oil to take up a large amount of oxygen before any considerable increase in its viscosity occurs. In the older processes, this limited the temperature for treating the oil to about 120–125°F.; higher temperatures, e.g., 140°F. or above, were said to yield an inferior product.

Originally, polymerized oil for the manufacture of linoleum was made by the "scrim" process, wherein lengths or scrims of light cotton fabrics were suspended in a warm room provided with air circulation and periodically (about every 24 hours) flooded with previously boiled oil. After about 3 to 6 months the fabrics became coated with a layer of polymerized oil about 1 inch thick, which was then stripped off. The scrim process is now largely superseded by the "smacker" process, in which the oil, heated to about 120°F., is stirred in a horizontal jacketed drum equipped with a horizontal agitator with radial arms or paddles, under a strong current of air. Before it is charged to the smacker, the oil may be previously oxidized to some degree by other means. Older practices in-

[1a] G. A. O'Hare, *J. Am. Oil Chem. Soc.*, *27*, 530–533 (1950).

cluded airblowing or spraying at a low temperature. A modern process,[2,3] which is much more effective, makes use of intensive mechanical agitation of oil and air in a machine of the turbo-gas-diffuser type.[3] In such an apparatus it is stated that the oxygen content of linseed oil can be increased from about 11% to 17–18% before the oil becomes highly viscous. Much higher temperatures (well above 200°F.) can be employed, and the reaction is completed within a few hours, or a small fraction of the time required for a comparable portion of the older processing cycle.

In the smacker, the oil is often mixed with a small quantity of whiting or other extender. The oil from the smacker is cooled and, after solidification, is cut up into chunks which are then stored or "stoved" for several days at about 100°F. During this period, the product becomes still stiffer and more crumbly, and swells to form a honeycomb structure from the generation of gases within the mass. Swelling will occur without the presence of whiting or other carbonate, and in improperly processed material may fail to take place in the presence of carbonate; hence it cannot be attributed to the generation of carbon dioxide from the latter.[4]

In the second step in the preparation of linoleum cement, the polymerized oil is fluxed with rosin or other resins. The resin mixture originally recommended consisted of equal parts of rosin and kauri gum, but the latter gum is now said to be often omitted.[5] Approximately 1 part resin is used to 4 parts polymerized oil. The oil and resins are heated together at about 275 to 300°F. until the desired degree of reaction and thickening have occurred. If kauri or other fossil gum is used, it is not previously "run," as in varnish making, to make it completely compatible with the oil, and although reaction takes place between the polymerized oil and the rosin, to yield a particular variety of thermoplastic resin, fossil gum or hard synthetic resins appear simply to stiffen the product mechanically.[4]

The final step in the development of the body of the finished material takes place after the linoleum is formed, when it must again be cured by "stoving" or "seasoning" at a moderately elevated temperature (150–200°F.) in large ovens for a period of several days or weeks.

Linoleum cement is not merely another form of infusible drying oil–resin polymer, similar to that in an ordinary dried varnish film. As pointed out by Miller and Snell,[5] in the manufacture of linoleum the separate processes of heat polymerization and oxidation polymerization are reversed from their usual order, as in the formation of protective coatings. It is particularly to be noted that linoleum cement is unlike a hardened paint or varnish film in that it is fusible and thermosetting. This prop-

[2] G. A. O'Hare and W. J. Withrow, *Ind. Eng. Chem.*, *39*, 101–104 (1947).
[3] E. Hazlehurst (to Congoleum-Nairn Inc.), U. S. Pat. 2,446,652 (1948).
[4] M. R. Mills, *private communication* (1946).
[5] A. B. Miller and F. D. Snell, *Ind. Eng. Chem.*, *25*, 1307–1311 (1933).

erty is important in its relation to the mechanism of linoleum manufacture. Fusibility in the cement is particularly essential in the manufacture of inlaid linoleum, as this process requires the welding together of many separate blocks of material, and the reworking of much scrap. In a few large modern plants inlaying is carried out by entirely automatic high-speed machinery.[1]

The chemistry of linoleum cement manufacture is even less well understood than that of ordinary polymerization processes involving a drying oil. The reaction occurring between the rosin and the polymerized oil in the fluxing operation has never been fully explained. The monofunctional character of the rosin is considered important[5]; presumably it modifies the polymerization of the glycerides in the oil, to preserve the heat-convertible nature of the product. Although rosin itself is not an altogether essential component, some such acidic material appears to be indispensable; a peptizing effect of the rosin acids on the drying oil gel is suggested.[4] The chemical aspects of linoleum making are discussed at length by de Waele.[6] The theories of this author, while now old, do not appear to have been greatly improved upon.

From a practical standpoint, the success of linoleum cement making largely depends, as stated above, upon the somewhat difficult matter of maintaining a high degree of oxidation polymerization in relation to polymerization through the influence of heat.

The consumption of the various drying oils in floor covering manufacture in the United States in 1948 is shown in Table 97.[1a]

TABLE 97

OILS USED IN MANUFACTURE OF FLOOR COVERINGS IN UNITED STATES IN 1948

Oil	Million lbs.
Soybean oil	22
Linseed oil	110
Tung oil	9
Castor oil	0.7
Fish oils	5
Other oils	0.3
Total	*147.0*

2. OILED FABRICS

There are two classes of oiled fabrics, consisting of those exemplified by ordinary "oilcloth," in which the oil forms a continuous coating on one side of the fabric, and those in which the entire fabric is impregnated with oil. Fabrics of the first class are used as coatings for walls, tables, shelves,

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[6] A. de Waele, *J. Ind. Eng. Chem.*, 9, 6–18 (1917).

and other surfaces which are not walked upon, or otherwise are not subjected to sufficiently severe abrasion to require a linoleum coating. Those of the second class are coated to make them water-repellent, and are chiefly used for raincoats, machine and instrument covers, etc. Both classes, but particularly the second class, must be pliable.

Oilcloth is made by applying successive coats of paints and varnishes to a cotton backing, with the final coat being designed to impart to the surface a high gloss. The paints and varnish must be compounded to produce a coating which will withstand moderate flexing without cracking, hence they cannot be made exclusively with highly drying oils, but must contain plasticizers.

Linens and silks are the fabrics which are usually oiled. The oiling operation consists merely of thoroughly impregnating the fabric with unpigmented drying oils, and allowing each application of the oils to dry thoroughly. Strongly drying oils such as perilla or tung oils are less suitable for this purpose than oils which yield softer and more pliable films, such as linseed and fish oils.

The cordage used in fishing nets, etc., is usually oiled, the oils most used for the purpose consisting of linseed oil and fish oils.

3. Putty and Other Sealing Materials[6a]

There are a variety of sealing materials and cements which have a drying oil base, of which ordinary window putty is the most common example. There was a factory production of 17,463 thousand pounds of this material in the United States in 1947. Putty is usually composed simply of a thick, plastic paste of whiting and linseed oil. Some sealing materials with a fatty oil base are treated to produce a rubberlike material. Others are more nearly like heavy paints or varnishes. The stearine pitch remaining from the distillation of fatty acids may be placed in this category of products; it is used in the manufacture of wall board, floor tiling, electrical insulation, industrial paints, and other products requiring a relatively high-grade pitchlike material.

4. Rubberlike Materials

Unsaturated fats and oils, and particularly the drying oils, are capable of polymerizing to form various elastic, rubberlike materials.

The oldest materials of this class are the *factices*, which are polymerized with the aid of sulfur. The action of sulfur is in this case entirely similar to its action in the vulcanization of rubber, *i.e.*, it modifies the structure of the polymer by providing a ready means of cross bridging through the sulfur molecules.

[6a] S. S. Gutkin, *J. Am. Oil Chem. Soc.*, *27*, 538–544 (1950).

There are two varieties of factice: *white* and *brown*. White factice is prepared by reacting a relatively saturated oil, such as castor or rapeseed oil, with liquid sulfur monochloride. The reaction takes place readily in the cold, and may be ideally represented as follows:

```
   H  H  H  H                              H  H  H  H
   |  |  |  |                              |  |  |  |
  —C —C=C—C—                             —C—C—C—C—
   |     |                                |  |  |  |
   H     H                                H  Cl |  H
                                                S
   H  H     H                             H  H  |  H
   |  |     |                             |  |  |  |
  —C—C=C—C—      +    S₂Cl₂    ⟶       —C—C—C—C—
   |     |  |                             |  |  |  |
   H     H  H                             H  |  H  H
                                             S
   H        H                             H  |  Cl H
   |        |                             |  |  |  |
  —C—C=C—C—                              —C—C—C—C—
   |  |  |  |                             |  |  |  |
   H  H  H  H                             H  H  H  H
```
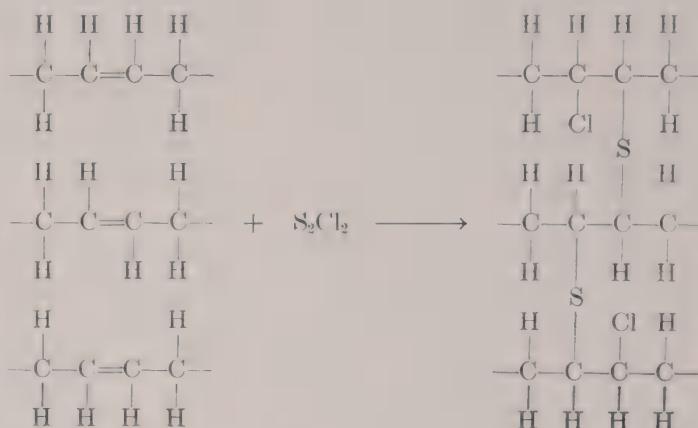
Actually, the reaction appears to be quite complex. Obviously, simple addition of sulfur and chlorine atoms at the double bonds can take place in a number of different ways, with each molecule of sulfur monochloride eliminating from one to three double bonds, hence there is no particular relation between the unsaturation of the oil and the amount of reagent absorbed. Substitution also appears to take place, since in some cases, particularly in the treatment of highly unsaturated fish oils, there is a considerable evolution of hydrogen chloride gas. For detailed discussion of the chemistry of factice manufacture, reference may be made to the publications of Kaufmann and co-workers.[7]

White factice is a light-colored, compressible, but more or less crumbly material, which is principally used as an extender or modifier for rubber.[8] An important use for this material· is in the manufacture of erasers, wherein it confers that degree of friability which is essential in this product.

Brown factice is made by first blowing a drying oil until it is thickened, and then reacting the partially polymerized oil with about 5–30% of its own weight of powdered elemental sulfur. The reaction is carried out in a closed vessel, with stirring, at a temperature of about 250–350°F., over a period of 1–2 hours. Depending upon the percentage of sulfur, the temperature and the reaction time, the product varies in consistency from

[7] H. P. Kaufmann, J. Baltes, and P. Mardner, *Fette u. Seifen*, *44*, 337–340 (1937); H. P. Kaufmann, E. Gindsberg, W. Rottig, and R. Salchow, *Ber.*, *B70*, 2519–2535 (1937).

[8] For a review of the use of factice as a rubber extender, see E. H. Hurlston. *Trans. Inst. Rubber Ind.*, *11*. 294–301 (1935); *Rubber Chem. Technol.*, *9*. 621–625 (1936).

a dark, viscous, and sticky semisolid, to a hard and relatively brittle solid. The characteristics desired will depend upon the specific use to which the factice is to be put. The chemical reactions taking place in the manufacture of brown factice are undoubtedly even more complex than those involved in making white factice, but again they may be likened to those occurring in the vulcanization of rubber.

Brown factice is used not only as a rubber extender, but also to modify the properties of drying oil products, as in varnishes, linoleum, etc.

Although somewhat rubberlike, none of the factices possesses the combination of great elasticity and high tensile strength of vulcanized natural rubber or its synthetic substitutes, because of the tendency toward polyfunctionality of all glycerides (see page 418), and the consequent production of an extensively cross-linked structure rather than the structure of long linear chains with occasional cross linking that is characteristic of so-called elastomers.

The essential linear polymer of high molecular weight can be constructed from fatty materials, *e.g.*, from dilinoleic acid esterified with a glycol or other dihydric alcohol[9]; hence by special techniques it has been found possible to make a fatty oil based product which resembles rubber to a large degree. This product was developed under the name of *Norepol*.[10] It was manufactured on a trial scale during the rubber shortage created by World War II, and would probably have found considerable use had linseed oil or soybean oil, the preferred raw materials, remained in good supply.

The first step in the manufacture of this material involves conversion of the polyfunctional glycerides to a monofunctional form by reaction of the oil with methyl alcohol or other monohydric alcohol, to yield monoesters. The latter are then heat-polymerized, the reactive esters principally forming dimers, and the nonreactive esters remaining as monomers. The latter are removed from the mixture by fractional distillation, and the monohydric alcohol attached to the dimeric residue is replaced with ethylene glycol. This product is then further polymerized, after which it may be vulcanized and compounded to yield the finished rubberlike material.

The products so far manufactured lack the tensile strength and abrasion resistance of natural rubber and some other synthetic products, but are satisfactory for most purposes where these properties are not of prime importance. They are particularly suitable materials for gaskets, stoppers, bumpers, tubing, electrical insulation, etc., and for the rubberizing of fabrics. Their resistance to oxidation is outstanding.

[9] J. C. Cowan and D. H. Wheeler, *J. Am. Chem. Soc.*, *66*, 84–88 (1944).
[10] J. C. Cowan, W. C. Ault, and H. M. Teeter, *Ind. Eng. Chem.*, *38*, 1138–1144 (1946).

5. Core Oils[6a]

Core oils are used as binding agents for the sand cores of hollow metal castings. The cores are prepared by mixing approximately 50 parts by volume of sand with 1 part of oil, molding the mixture in a wooden form and baking at a temperature of about 400° to 450°F. until a hard, coherent mass is formed. The sand is usually dampened to make it more easily molded, and a water-soluble binder, such as casein, dextrin, etc., is sometimes added to assist in maintaining the core in the proper form until it becomes hardened through heat polymerization of the oil.

The core should have sufficient mechanical strength to retain its form during the casting operation, but should of course not be so hard as to be difficult to break and remove from the finished casting. It must have a certain degree of permeability, to permit the escape of gases evolved during casting. Test specimens baked and tested in an ordinary cement tester should have tensile strengths of the order of 200 lbs. per square inch.

The oils used in core making include linseed, soybean, tung, fish, and esterified tall oils. They are usually bodied to a viscosity of A–G, and are used without dryers.

6. Tanning Oils

In the operation of oil tanning, the skins are impregnated with a suitable drying oil, and stored at a warm temperature (*e.g.*, 100°F.) until considerable oxidation of the oil has taken place. The excess of oil is then removed by scouring. Tanning occurs as the result of chemical combination of aldehydes or other products of oxidation with the collagen of the skins. In the process a sufficient amount of oil or of long chain glyceride fragments is fixed to make the finished leather very soft and pliable.

Oil tanning is employed in the tanning of furs, and also for making chamois and other washable leathers, for gloves, etc.

The oils used in tanning consist exclusively of marine oils, of which cod oil appears to be particularly preferred. The particular desirability of marine oils is attributed by Dean[11] to the fact that they contain substantial proportions of both highly unsaturated acids and acids relatively lacking in unsaturation. Since the fatty acids tend to be evenly distributed in the glyceride molecules, the average molecule will thus contain both highly unsaturated acids, to make it oxidizable and reactive with the leather, and saturated or monoethenoid acids, to remain unoxidized and contribute a lubricating action.

[11] H. K. Dean, *Utilization of Fats.* Chemical Pub. Co., New York, 1938, p. 277.

B. Lubricants and Plasticizers

1. LUBRICATING OILS

Although fatty oils were once extensively used as lubricants for machinery, they are now largely supplanted by mineral oils. The latter do not hydrolyze and thus become acid and corrosive in use, and in addition they are cheaper than fatty oils. However, fatty oils have certain special advantages, which have insured their continued use in limited quantities. The principal virtue of these oils as lubricants results from their superior ability to cling to metal surfaces in the form of very thin films. Actually, this property appears to be largely due to the surface activity conferred by the small amount of free fatty acids occurring in the oils[12]; the free acids are polar in nature and tend to become adsorbed in layers of molecular dimensions at the metal–oil interface. The interposition of such films is effective in preventing metal seizure under conditions of extreme pressure, or under other conditions tending to displace gross films of lubricant between the bearing surfaces. Fatty oils are also less easily displaced from metal surfaces by water than are mineral oils, and hence are valuable ingredients for lubricants designed for the cylinders and valves of steam engines.

Sulfurized fatty oils are sometimes added to lubricants simply for the sake of the sulfur that they carry. This is particularly practiced in the case of cutting oils and extreme-pressure lubricants. It is considered that the sulfur prevents contact between closely opposed ferrous metal surfaces through the interposition of a film of iron sulfide.

Fatty oils are used in some quantity for the lubrication of very light machinery and delicate mechanisms, such as watches, clocks, scientific instruments, spindles, looms, sewing machines, etc. The oils which are suitable are those which are sufficiently saturated to be free from gumming tendencies, yet which are liquid at ordinary temperatures. These include lard oil, neatsfoot oil, and sperm oil, the latter of course, being actually a liquid wax rather than an oil. Olive oil belongs to the class of liquid, nongumming oils, but is little used as a lubricant because of its high price.

Castor oil is more viscous than ordinary oils, and hence is suitable for lubricating fairly heavy machinery. Its viscosity changes relatively little with temperature, and it has a low cold test or solidifying point (ca. 0°F.); hence it was once considered more or less essential for the lubrication of

[12] For a complete discussion of the function of surface-active compounds in lubricants, see G. L. Clark, B. H. Lincoln, and R. R. Sterrett, *Proc. Am. Petroleum Inst.* *III. 16,* 68–80 (1935).

airplane engines. In this and similar applications it has now been replaced almost altogether by the newer low cold test mineral oils.

There is a considerable production of blended oils, comprised of mineral oils containing a fatty oil. "Blown" rapeseed oil or rapeseed oil which has been thickened by polymerization, is a particularly common ingredient of such products. It not only contributes surface-active properties to the blend, but also increases the viscosity of the mineral oil. Blends containing from about 5 to 25% of fatty oil are particularly used for machinery operating under heavy loads, or at high temperatures, such as marine and Diesel engines. The blends are less easily washed away from metal surfaces by water and steam than ordinary mineral oils, and hence are preferred for the lubrication of steam engines. Low-acid lard and tallow oils are also much used in compounding.

The well-known "germ" process of Southcombe and Wells[13] for improving lubricating oils originally embodied incorporation of a small amount, e.g., 0.5%, of a fatty acid. However, certain chlorinated fatty acid derivatives[14] appear to be superior to simple fatty acids for this purpose.

2. LUBRICATING GREASES

Many mechanical devices are constructed in such a manner that they cannot be conveniently or efficiently lubricated by a liquid oil, but require a semisolid, plastic lubricating grease. These greases consist of lubricating oils stiffened by the addition of various soaps.

Lubricating greases are prepared by heating a mixture of lubricating oil and soap to a high temperature, to form a homogeneous solution, and then cooling the mass with continuous agitation. Soap separates upon cooling in the form of curd fibers, and neat soap or other liquid crystalline material and, being intimately dispersed in the oil, forms with the latter a plastic solid. The characteristics of the finished greases depend upon the mineral oil used, the relative proportions of oil and soap, the fatty materials going to make up the soap, the metal used for forming the soap, the degree to which the soap is hydrated, and the method of solidifying the grease. In addition, certain minor constituents or additives, including glycerol from soaps formed in situ, may greatly influence the physical structure of the product. The diverse lubrication requirements of modern machinery make the technology of these products highly involved. It will be impossible to present here more than a bare outline of the subject.[15]

[13] J. E. Southcombe and H. M. Wells, U. S. 1,319,129 (1919; Brit. 130,877 (1918).
[14] L. L. Davis, B. H. Lincoln, and B. E. Sibley, Proc. Am. Petroleum Inst. III, 16, 81–103 (1935). B. H. Lincoln, G. D. Byrkit, and W. L. Steiner, Ind. Eng. Chem., 28, 1191–1197 (1936).
[15] For detailed information on the technology of lubricating greases, see the monograph of E. N. Klemgard, Lubricating Greases: Their Manufacture and Use. Reinhold, New York, 1937. For a recent short summary of practices and trends in the industry, see C. W. Georgi and J. B. Stucker, J. Am. Oil Chem. Soc., 24, 15–18 (1947).

The total production of lubricating greases in the United States was estimated[16] in 1947 to be not less than 500 million pounds annually. The corresponding consumption of fatty materials was estimated to be about 60 million pounds. The principal fatty raw materials are inedible tallows and greases. Lesser amounts of hydrogenated fish oils (usually in the form of fatty acids) are also consumed, as well as minor quantities of other oils. A considerable proportion of the total quantity of fats is used in the form of the separated fatty acids, including commercial oleic and stearic acids. Statistics are available on the total amounts of the different fatty materials used by petroleum refiners (Table 98), but not on the amounts entering separately into lubricating greases, lubricating oils, and other products.

TABLE 98

FACTORY CONSUMPTION OF FATS AND OILS IN MANUFACTURE OF LUBRICANTS
IN UNITED STATES DURING YEAR BEGINNING JULY 1, 1942[a]

Fat or oil	Million lbs.
Tallow	25.6
Greases[b]	19.0
Rapeseed oil	13.7
Marine animal oil	6.4
Wool grease	4.7
Fish oils	2.0
Soybean oil	1.2
Cottonseed oil	1.1
Linseed oil	1.0
Castor oil	0.8
Other vegetable oils	0.9
Other animal and marine oils	0.1
Total	*76.5*

[a] U. S. Bur. Census reports.
[b] Including a small amount of lard.

The metallic portion of the soap generally consists of sodium, calcium, or aluminum. Recently lithium stearate greases have attained considerable popularity, and there is also a small production of barium greases. Lead soaps are incorporated in certain types of greases, but for their lubricating value, rather than their stiffening effect. In addition to mineral oil and soaps, greases may also contain such ingredients as asphalt, petrolatum, mineral wax, rosin, dyeing and perfuming substances, and inorganic materials, including graphite, and other nonabrasive solids. If a fat rather than a fatty acid is used in forming the soap, and saponification is carried out directly in the mineral oil, as is often the practice, glycerol from the fat will remain in the grease. In some cases, particularly in that of calcium

[16] Georgi and Stucker, see footnote 15.

soap greases, considerable unreacted fat may remain in the grease, as well as substantial amounts of free alkali; a minor proportion of a fatty oil is occasionally added. A small amount of water is commonly associated with the soap.

The consistency of a lubricating grease will depend much more upon the amount of soap incorporated than the viscosity of the mineral oil. Often a series of greases of widely varying consistency is prepared from a single mineral oil, by simply using different proportions of soap. Thus, for example, ordinary calcium-base cup grease may contain from about 7% soap in the No. 00 grade to about 35% soap in the No. 6 grade. This is the ordinary range of soap content in most greases, although considerably less soap may be used where the object is merely to thicken a fluid oil, and very stiff, high-melting greases designed for service at high temperatures, such as locomotive driving journal compounds, may contain 50% or even 60% soap.

The body characteristics of lubricating greases are naturally related in an intimate way to the crystal or gel structure of the soap phase. Farrington and Davis,[17] as a result of microscopic study of greases, have proposed a classification of these materials upon the basis of the average length of their soap fibers, as follows:

Type	Fiber length, microns	Character
Long fiber	100 or more	Fibrous, ropy
Medium fiber	10 to 100	Clinging, slightly rough
Short fiber	1 to 10	Slightly rough, short
Microfiber	Less than 1	Smooth, unctuous

According to Farrington and Davis,[17] the suitability of greases for specific uses can be correlated with fiber length. Thus long-fiber greases are particularly adapted to use in gear boxes, since they are readily worked between the moving parts by the action of the gears, and they tend to take up the slack in worn gears and eliminate noise. Also they are easily retained within a gear housing. On the other hand, greases of this type are not good lubricants for ball and roller bearings, since they do not cling well to the balls and rollers. Short-fiber greases are the most suitable for locomotive journals and open-type roll bearings, whereas cup greases are always of the microfiber type.

Long-, medium-, and short-fiber greases are made with sodium soaps, with the fiber length generally tending to become greater as the fat stock becomes higher in iodine value and less saturated. The presence of water, glycerol, or other polar compounds also facilitates the production of long fibers.

Calcium, aluminum, and lithium greases are usually classed as "micro-

[17] B. B. Farrington and W. N. Davis, Ind. Eng. Chem., 28, 414–416 (1936).

fiber" products, although actually the stiffening agent in these consists largely of a liquid crystalline phase, and in some cases, at least, crystals or crystallites appear to be absent altogether.

In addition to the consistency at ordinary temperatures, the factors of resistance to high temperatures and to water are important. Sodium greases have a high melting point (usually above 300°F.), but comparatively poor water resistance, whereas calcium and aluminum greases are characterized by good water resistance, but a low melting point (below 200°F.). The increasing popularity of the newer lithium and barium greases is due to their combination of good heat and water resistance. Sodium greases are commonly made by saponifying the fat with caustic soda in open kettles in the presence of a portion of the mineral oil, heating to drive off excess water and produce a relatively dry soap, and then working in the remainder of the mineral oil, and cooling. Calcium soaps are processed similarly, using hydrated lime as the saponifying agent, and carrying out the reaction in a closed kettle under pressure at a moderately elevated temperature (ca. 300°F.). In both cases, it is preferred to have most of the fat consist of glycerides rather than free fatty acids, as the presence of glyceride liberated by saponification contributes to the desired physical properties of the finished grease. On the other hand, preformed soaps, usually of stearic or other saturated fatty acids, are used in making both aluminum and lithium soaps. The soap is dissolved in the heated oil (300–400°F.), and the technology of the process consists simply in cooling and working the product in such a manner as to obtain the finished product in the proper physical condition.

Metallic soaps in nonaqueous solvents, like sodium and potassium soaps in water, exhibit a highly complex phase behavior; hence the consistency, stability, and other physical properties of greases depend to a very large degree upon details of the operations of cooling and working. For discussion of the relation of these to metallic soap phases and to the presence of glycerol or other additives, reference may be made to the publications of Lawrence,[18] Smith,[19] and Puddington and co-workers.[20]

Continuous methods have been devised and successfully used for the manufacture of calcium, lithium, and other greases.[21] Because of their

[18] A. S. C. Lawrence, *Trans. Faraday Soc.*, *34*, 660–677 (1938); *J. Inst. Petroleum Tech.*, *24*, 207–220 (1938).

[19] G. H. Smith, *J. Am. Oil Chem. Soc.*, *24*, 353–359 (1947).

[20] W. Gallay and I. E. Puddington, *Can. J. Research*, *B21*, 202–229 (1943). W. Gallay, I. E. Puddington, and J. S. Tapp, *ibid.*, *B21*, 230–235 (1943); *B22*, 66–75 (1944). W. Gallay and I. E. Puddington, *ibid.*, *B22*, 90–108 (1944). F. W. Southam and I. E. Puddington, *ibid.*, *B25*, 121 (1947).

[21] H. G. Houlton, B. D. Miller, P. A. Lenton, J. A. Taylor, and B. E. Adams, *Oil & Soap*, *21*, 258–263 (1944). H. G. Houlton, A. E. Calkins, and A. Beerbower, *Chem. Eng. Progress*, *43*, 399–404 (1947). H. A. Woods, W. J. Yates, L. Klingen, and R. C. Barton (to Shell Development Co.), U. S. Pat. 2,468,799 (1949).

closer control over the variables mentioned above, they are claimed to yield products of better and more uniform quality than the older batch methods.

3. Cutting Oils

Cutting oils are used for the lubrication of tools for the cutting or machining and also for the stamping and drawing of brass and other metals. In some cases the oils are used as such, and in others they are employed in the form of an emulsion with water. The cutting fluid not only performs a lubricating function, permitting the tool to slide between the cutting and the face of the machined member with a minimum of friction, but also cools the tool, and washes away chips and particles of detached metal.

The standard cutting oil of the nonemulsifying type was for many years lard oil. The No. 1 or No. 2 grades with a free fatty acid content of 15–25% are the ones usually used. Ordinary mineral or paraffin oil is quite inadequate as a substitute for lard oil, but satisfactory products containing a minimum quantity of fatty oil are now prepared by compounding a sulfurized fatty oil with mineral oil. Oils of this type are principally used for thread cutting and similar applications where a heavy cut is taken at a relatively low speed.

For high-speed cutting, where frictional heat is generated rapidly, an emulsion-type cutting liquid is usually employed. The nonaqueous base for a liquid of this type may consist substantially of soap, a sulfonated oil, or a mixture of mineral oil with sulfonated oil or soap.

Wire-drawing compounds, stamping compounds, etc., may logically be classed with the above materials. These usually have a soap base, but require a fatty oil, such as blown fish oil in addition to mineral oil to give them the desired properties.

4. Oils for Leather Treatment[22]

The fibers of finished leather must be lubricated with a thin coating of oil, to enable them to slide readily over one another as the material is flexed. The liquid oils which are most used in leather treatment are neatsfoot oil and fish oils, particularly cod oil. Tallows and greases are the plastic fats usually employed. There is also some use of waxes, such as wool grease, beeswax, and carnauba wax, as well as paraffin wax and mineral oils.

Light leathers are usually oiled by the so-called fat-liquoring process, wherein the skins are tumbled in a drum containing a dilute emulsion of

[22] For detailed information on the oiling of leather, see J. R. Blockey, *The Application of Oils and Greases to Leather*. Shoe and Leather Reporter Co., Boston. 1919.

oil and water stabilized by a sulfonated oil. The sulfonated oil serves to carry the oil to the interior of the skins, where it is deposited by subsequent breaking of the emulsion. Heavier leathers are oiled by the hand stuffing process, in which the damp leather is smeared with a plastic grease or "dubbin," consisting typically of a mixture of tallow and cod oil. The high-melting fat in this composition is not absorbed, but serves merely as a vehicle for the liquid oil and is removed at the conclusion of the operation. If it is desired to cause the leather to absorb higher melting fats or waxes, it may be "drum-stuffed," by tumbling the wet leather in a drum with the melted fat. Other methods of incorporating the oil are by "burning-in," or applying the hot melted fat by hand to the dry leather; and dipping the leather in the melted fat. The latter methods are principally employed where it is desired to impart some degree of water-proofness to the material.

In all methods of oiling leathers, the distribution of oil is assisted by the action of water. One function of the water appears to be to cause the leather fibers to spread and separate. The presence of water also favors the spreading of oil films on the fibers, in some manner as yet but little understood. In the methods mentioned above in which oil or fat is applied to the dry leather, the oiled leather is later drummed with warm water, to distribute the fat.

The grain surface of wet vegetable tanned leather is "oiled-off" by the application of a thin oil coating before the leather is dried, to lubricate the grain, and to permit the leather to dry without the concentration of tanning liquors at the surface. Some leathers, e.g., sole leather, receive little or no oiling except in this operation.

In the lubrication of leathers the chemical reactivity of the fatty oils is important, hence mineral oils are not suitable substitutes. The action of leather treating oils is not purely physical; some degree of chemical combination apparently occurs between the leather and the oil since the latter is not readily removed after it is once incorporated, even upon treatment with solvents.

5. TEXTILE LUBRICANTS

Textile lubricants are used for rendering textile fibers pliant, and enabling them to move smoothly over one another in the operations of combing, spinning, weaving, etc. Any lubricants applied to the fibers in the course of processing must of course be removed from the finished textiles. Fatty oils are much more easily removed than mineral oils, and in addition are superior lubricants; hence they are used almost exclusively for this purpose.

Sulfonated oils of various types are principally used as lubricants for cotton textiles and the various synthetic fibers, but there is some use of

straight oil, usually neatsfoot oil, lard oil, or inedible olive oil, as a worsted lubricant. Other liquid oils of a more unsaturated nature are not suitable substitutes, since they are inclined both to gum and to undergo rapid oxidation after application, with generation of heat and consequent hazard of spontaneous combustion.

6. Plasticizers

Whenever a fatty material is incorporated into a composition for its plasticizing effect, its function may be considered essentially one of lubrication. The fatty materials used as plasticizers consist of both fats and fatty acids. Of the former, castor oil is a particularly valuable agent, as its content of hydroxy acids enables it to be incorporated in products with which ordinary fats and oils are incompatible.

Fatty plasticizers are used in a very wide variety of materials, including rubber, nitrocellulose, and many synthetic plastics.

C. Miscellaneous Nondrying Oil Products

1. Illuminants and Fuels

Fatty oils were once widely used as burning oils for illumination, but have been entirely replaced by cheaper petroleum products except for a few highly specialized uses, and in isolated regions where petroleum is not available.

There is still some small production of a special burning grade lard oil, which is claimed to keep signal lights in operation for longer periods without adjustment or trimming of wicks than the usual petroleum oils.

Because of their ornamental value and their use for votive purposes and special occasions, there is still a considerable manufacture of candles the world over.[23]   Although the basic materials for candles consist of paraffin wax and beeswax, candles made from these materials alone are not sufficiently high melting to maintain their shape well in hot weather or to burn without excessive dripping. Stearic acid has long been the standard hardening agent for candles, and since the advent of the hydrogenation process there has also been considerable use of very highly hydrogenated fats for this purpose, either as such or more usually in the form of their fatty acids.

The amount of stearic acid or other fatty hardener used in candles depends upon the type of candle and the other ingredients; it may be as little as 5%, or as much as 50% or more.

[23] For information on candle manufacture, see E. Schlenker in *Chemie und Technologie der Fette und Fettprodukte*, H. Schönfeld, ed., Vol. II, Springer, Vienna. 1937; and also L. W. Geller, *Oil & Soap*, **12**, 262–265 (1935).

Palm oil and other fatty oils have been used as Diesel engine fuels. There is a considerable literature on the pyrolysis of fats to produce light motor fuels, and during periods when petroleum was not available, plants have actually been operated in China. In general, calcium or other soaps appear to be better materials for pyrolysis than the fat itself, although the latter may be cracked under pressure. From a ton of tung oil Chang and Wan[24] have reported the production *via* calcium soaps of 60 gallons of gasoline and either 0.73 ton of Diesel oil or 0.6 ton of Diesel oil and 40 gallons of kerosene. The pyrolysis of soybean oil soaps has been described by Sato and co-workers,[25] and of fish oil soaps by Arnoux.[26] Egloff and co-workers[27] have described experiments in which cottonseed oil and seal oil were cracked under pressure to produce 58–60% of a low octane value gasoline.

Mandlekar and co-workers[28] have described a process whereby fats are thermally cracked in the vapor phase at 535°C. to produce a fuel gas. In a typical example, peanut oil was made to yield a gas with a heating value of 550 Btu.'s per cubic foot, which contained over half the calorific value of the original oil. Its carbon dioxide content was but 3.6%, the remainder consisting of carbon monoxide, hydrogen, and saturated and unsaturated hydrocarbons.

"Napalm," the material used on a very wide scale during World War II as a gelling and thickening agent for gasoline in the manufacture of incendiary bombs, consisted of mixed aluminum soaps of naphthenic, oleic, and coconut oil fatty acids.[29]

2. Cosmetic and Pharmaceutical Oils

In cosmetics as in many other products, petroleum fractions have taken over many of the traditional functions of fatty oils. However, oils, fats, and fatty acids are still important materials in the cosmetic and pharmaceutical industry.

Fats in the form of almond oil, olive oil, palm oil, hydrogenated lard, etc., are used in the treatment type of creams, ointments, and lotions, since they are more readily absorbed by the skin than mineral oils. Vanish-

[24] C. Chang and S. Wan, *Ind. Eng. Chem.*, *39*, 1543–1548 (1947); see also C. Chang, *Chem. & Met. Eng.*, *52*, No. 1, 99 (1945).
[25] M. Sato and H. Matsumoto, *J. Soc. Chem. Ind. Japan*, *30*, 242–252 (1927).
[26] J. Arnoux, *Ann. musée colonial Marseille*, *9*, No. 1, 1–13 (1941).
[27] G. Egloff and J. C. Morrell, *Ind. Eng. Chem.*, *24*, 1426–1427 (1932). G. Egloff and E. F. Nelson, *ibid.*, *25*, 386–387 (1933).
[28] M. L. Mandlekar, T. N. Mehta, V. M. Parekh, and V. B. Thosar, *J. Sci. Ind. Research India*, *B5*, 45–47 (1946).
[29] L. F. Fieser, G. C. Harris, E. B. Hershberg, M. Morgana, F. C. Novello, and S. T. Putnam, *Ind. Eng. Chem.*, *38*, 768–773 (1946).

ing creams, foundation creams, powder bases, etc., are basically similar to brushless shaving creams, i.e., they consist of an emulsion with a base of incompletely saponified stearic acid.

Castor oil is used in hair dressings because of its property of mixing freely with alcohol. It is also used as a plasticizer in nail polishes.

Stearic acid in the form of zinc, calcium, and magnesium stearate is much used in face, bath, and talcum powders.

Many cosmetic preparations contain fats in the form of soaps, sulfonated oils, and various emulsifying agents.

Edwards[30] lists the following fats, oils, fatty acids, and waxes which are official with the *United States Pharmacopoeia* and the *National Formulary:*

Oleum Amygdalae Expressum u.s.p. (expressed oil of almond), Oleum Chaulmoograe u.s.p. (chaulmoogra oil), Oleum Gossypii Seminis u.s.p. (oil of cottonseed), Oleum Lini u.s.p. (linseed oil), Oleum Maydis u.s.p. (corn oil), Oleum Morrhuae u.s.p. (cod liver oil), Oleum Olivae u.s.p. (olive oil), Oleum Ricini u.s.p. (castor oil), Oleum Sesami n.f. (sesame oil), Oleum Tigilii n.f. (croton oil), Acidum Oleicum u.s.p. (oleic acid), Acidum Stearicum u.s.p. (stearic acid), Adeps (lard), Adeps Benzoinatus (benzoinated lard), Adeps Lanae (wool fat), Adeps Lanae Hydrosus (hydrous wool fat or lanolin), Oleum Theobromatis (cocoa butter), Sevum Preparatum (prepared suet), Cera Alba (white wax), Cera Flava (yellow wax) and Cetaceum (spermaceti) are all u.s.p. materials.

In pharmaceutical preparations, oils and fats are used as emollients, and as carriers for medicinal substances to be applied to the skin. Castor oil and croton oil are used as cathartics, and chaulmoogra oil is used in the treatment of leprosy. The use of cod liver oil and other fish liver oils as sources of vitamins A and D is of course well known. Oils such as corn oil, sesame oil, and cottonseed oil are employed as carriers for vitamin concentrates and other fat-soluble substances.

Until quite recently, fish liver oils were the sole source of vitamin A concentrates. Now, however, synthetic vitamin A preparations are available cheaply and in quantity,[30a] and it may be expected that eventually they will largely supplant the natural products, at least for human consumption.

Cocoa butter has the property of remaining firm at ordinary temperatures, but melting at the temperature of the body, hence is a standard base for suppositories.

[30] L. D. Edwards, *Oil & Soap, 17,* 82–84 (1940).
[30a] See, for example, J. A. O'Connor, *Chem. Eng.,* No. 4, 146–147 (1950).

3. Tinning Oils

Normally, from 20 to 40 million pounds of palm oil are used annually in the United States in the manufacture of tin plate and cold-reduced sheet steel.

In tin plating, a thick layer of the oil is placed over the molten tin in the exit section of the plating bath to protect the tin from oxidation. The oil also absorbs metallic oxides and flux residues, and serves to maintain the tin coating in a molten condition as the metal sheets emerge from the metal bath; it thus assists in producing upon the sheets a uniform coating. In terne plating, from a tin–lead bath, a coating of oil serves a similar purpose, although some terne plating is carried out in a single bath with only a flux covering the molten metal.

In the cold reduction process, the oil serves simply as a lubricant.

Crude palm oil is used to the practical exclusion of other oils in tinning because it is relatively cheap, and has a composition near the optimum for the purpose. The oil used must not be very unsaturated, else it will polymerize too rapidly at the high temperature (460–550°F.) of the bath. On the other hand, a certain degree of heat degradation in the oil is desirable, since it produces free fatty acids and possibly other compounds which assist in dissolving metallic oxides, and promote uniform wetting of the metal by the oil. Recently, uncertainties in the supply of palm oil in the United States have prompted a search for substitutes. Materials which have undergone successful mill tests include a mixture of dimerized linoleic acid (see page 883) and its monohydric alcohol ester, steam-refined tallow fortified with a controlled amount of free fatty acids, and a mixture of the monohydric alcohol esters of a marine oil with hydrogenated glycerol esters.[31]

4. Hydraulic Oils

Castor oil is extensively used as a base for fluids for hydraulic systems, and particularly those exposed to low temperatures, for example, automobile brake systems and those used for various purposes on airplanes. Castor oil has certain advantages over mineral oils and other fatty oils; it has a relatively low cold test, is compatible with polar liquids of low viscosity, and has little effect on rubber gaskets.

The compounding of castor oil-base hydraulic fluids is discussed by Shough,[32] who recommends higher aliphatic alcohols as the other principal

[31] G. G. Ference, W. R. Johnson, L. C. Kinney, and J. M. Parks, *J. Am. Oil Chem. Soc.*, **27**, 122–127 (1950).
[32] A. H. Shough, *Ind. Eng. Chem.*, **34**, 628–632 (1942).

ingredient, and the use of bodied, rather than raw, castor oil, to obtain a mixture of reasonably high viscosity, but low cold test.

5. INSECTICIDES AND FUNGICIDES

Fatty oils are used in insecticide sprays in the form of soaps or other surface-active materials, as wetting and spreading agents. Oils as such are used to promote adhesion of the spray in the "inverted-spray" method of Marshall[33] for the control of the codling moth. The oils employed are exclusively fish oils, principally because of the low cost of these.

In some cases fats or fatty derivatives may in themselves be toxic agents for insects. Soaps have been found to be effective against some insects,[34] although in practice they are used only as adjuncts to other and more potent insecticides. Ralston, Barrett, and Hopkins[35] have found certain fatty amines to be effective against houseflies, and have suggested dioctyl amine as a substitute for pyrethrum in household insect sprays. Sesame oil is used as an addition agent to pyrethrum-based insect sprays because of the synergistic action of its unsaponifiable materials.[36]

Fatty oils, and particularly fish oil, are used in the preparation of sticky, weatherproof, tree-banding compounds, used to prevent infestation of trees by larvae from the ground.

Commercial stearic acid with a very low content of unsaturated acids is used in the manufacture of a new fungicide for fruit trees.[36a]

D. Commercial Fatty Acids and Their Derivatives

Although the characteristics and uses of the commercially available fatty acids are mentioned in various other places in this book, it appears desirable to make a recapitulation here of the data pertaining to this important class of fatty materials, as well as certain derivatives which are produced and marketed in sufficient quantity to be well-recognized commercial products.

1. COMMERCIAL STEARIC AND OLEIC ACIDS

The products commonly known as oleic and stearic acids have for many years been made by fractionally crystallizing and pressing the mixed fatty acids from inedible tallow. This operation merely produces a reasonably

[33] J. Marshall, *Wash. Agr. Expt. Sta., Tech. Bull.* No. 350, 1–88 (1937).
[34] F. Tattersfield and C. T. Gimingham, *Ann. Applied Biol., 14*, 217–239 (1927). W. E. Fleming and F. E. Baker, *J. Agr. Research, 49*, 29–38 (1934).
[35] A. W. Ralston, J. P. Barrett, and E. W. Hopkins, *Oil & Soap, 18*, 11–13 (1941).
[36] H. L. Haller, E. R. McGovran, L. D. Goodhue, and W. N. Sullivan, *J. Org Chem., 7*, 183–184 (1942).
[36a] H. W. Thurston, Jr., *Agr. Chemicals, 5*, 28–31, 99 (1950).

close separation of the saturated and unsaturated acids in the mixture; hence these acids are by no means pure or even fairly pure compounds. Actually, commercial stearic acid contains slightly more palmitic acid than stearic, the ratio of the two acids being about 55 to 45. In addition to these two saturated acids, it also contains from 2 to 8% unsaturated acids, consisting principally of oleic, with a small amount of linoleic acid. Commercial oleic acid usually contains not more than about 70% actual oleic acid, the impurities consisting of the above-mentioned saturated acids and linoleic acid, in approximately equal proportions, plus 2–5% of unsaponifiable matter.

Stearic and oleic acids are made in so-called saponified and distilled grades, according to whether the fatty acid stock is taken directly from the splitting equipment, or distilled before pressing. Considerable purification of the acids is obtained by distilling; on the other hand, saponified acids are usually made from higher grade materials than distilled acids, and are not necessarily inferior in quality.

In 1947 the United States Bureau of the Census reported the manufacture of 70,405 thousand pounds of oleic acid, and 60,227 thousand pounds of stearic acid.

Stearic acid is single-, double-, or triple-pressed, according to the hardness and degree of unsaturation desired. Average melting points of single-, double-, and triple-pressed stearic acids are respectively about 126–127°, 128–129°, and 130–131°F. Iodine values of the three grades average about 12, 7, and 5, respectively, whereas average titers are approximately 53.2°, 54.2°, and 55.2°C. Good stearic acid is white or only slightly yellowish in color, has a characteristic tallowy, but not strong odor, and is pulverulent and only slightly waxy in consistency. It shrinks markedly upon solidification.

Oleic acid, otherwise known as *red oil*, is normally colored to some degree; the color of the best products is similar to that of refined but unbleached vegetable oils, *e.g.*, 35 yellow and 8–10 red on the Lovibond scale, but much is a deep red or reddish brown. The color depends to a large degree upon how much the product has been contaminated with iron. With prolonged heating in ordinary carbon steel containers it will become almost black; special light grades with a Lovibond color in the neighborhood of 15 yellow and 1.5 red are shipped in aluminum drums or tank cars.

The iodine value of commercial oleic acid is usually between about 88 and 93, and often is quite close to 90, which is the iodine value of pure oleic acid. However, this is only because considerable amounts of linoleic acid and of saturated acids and unsaponifiable matter are present in approximately equal proportions. The titer is ordinarily a little below

that of pure oleic acid, or about 10°C. Special grades are available in which the saturated acids have been reduced by recrystallization to lower the titer to about 3–5°C. and increase the iodine value to 93–95.

2. OTHER FATTY ACIDS

Demands upon the part of industry for a greater diversity of materials and the development of new processing techniques have combined in recent years to make available many grades of fatty acids other than the traditional "stearic acid" and "red oil" described above. In 1947 the United States Bureau of the Census reported a factory production of 272,893 thousand pounds of such products. Whereas the old pressing method was confined essentially to animal fats containing palmitic and stearic acids in the approximate ratio of 55 to 45, it is possible to produce saturated fatty acids with these two acids in entirely different proportions by the newer methods of solvent crystallization.[37] Vegetable oil fatty acids, usually derived from the soapstock produced by alkali refining are available as such, and in hydrogenated forms of very high titer. Soybean oil fatty acids are in particular demand for the manufacture of oil-modified alkyd resins. Fatty acids from fish oils or from such vegetable oils as cottonseed or soybean are distilled to produce fractions high and low in iodine value, and coconut or palm kernel oils are similarly distilled to separate fractions of high and low molecular weight.

By distillation of saturated acid mixtures through efficient fractionating columns it is possible to obtain cuts consisting substantially of a single fatty acid. One manufacturer has for a number of years offered products of the following specifications[38]: Stearic acid: iodine value, 3.0; mean molecular weight, 282.5; titer, 67.0°C.; contains 90% stearic acid, 6% palmitic acid, and 4% oleic acid. Palmitic acid: iodine value, 3; mean molecular weight, 258; titer 56°C.; contains approximately 90% palmitic acid, 6% stearic acid, and 4% oleic acid. Myristic acid: iodine value, 2; mean molecular weight, 226; melting point 51°C.; contains 90% myristic acid, 4% lauric acid, 4% palmitic acid, and 2% unsaturated acids. Lauric acid: iodine value, 1; mean molecular weight, 203; titer, 37.8°C.; contains 90% lauric acid, 9% myristic acid, a trace of capric acid, and 1% unsaturated acids. Capric acid: iodine value, 1.2; mean molecular weight, 173.3; melting point, 30°C.; contains 90% capric acid, 7% lauric acid, 3% caprylic acid, and a trace of unsaturated acids. Caprylic acid: iodine value, 0.8; mean molecular weight, 145.7; melting point 13.0°C.; contains 90% caprylic acid, 3% caproic acid, 7% capric acid, and a trace of unsaturated acids.

[37] Emeryfacts, Emery Industries, Inc., 1943, revised 1948.
[38] Neo-Fat: New Fatty Acids and Oils for Industrial Purposes. Armour and Co., 1945. Chemicals from Fats; Fatty Acids and Their Derivatives, Armour & Co., 1949.

Unsaturated fatty acids composed substantially of oleic and linoleic acids, presumably derived from cottonseed oil foots, are sold in considerable quantities for incorporation into non-yellowing alkyd resins.

A very recent development by one American manufacturer is a new line of "stearic acids" of exceptionally high purity, i.e., with an iodine value not in excess of 0.5 and with a content of unsaponifiable matter not exceeding 0.2%.[38a] One of the results of their high purity is extremely low color combined with remarkable color stability. They are available with varying percentages of true stearic acid.

Another recent development is a commercial oleic acid which is substantially linoleic-free, and consequently of very high stability.[37]

In addition to the more or less special fatty acids mentioned above, the mixed fatty acids from almost any common oil or fat are available commercially. In a few special cases, such as that of large-scale continuous soap manufacture, plants are set up so that the processing step utilizing fatty acids is immediately preceded by stages of fat splitting and distillation. Usually, however, the production and utilization of fatty acids are in different establishments.

The recent trend has been toward the production of fractionated fatty acids comprising relatively close cuts with respect to chain length and more particularly, degree of unsaturation, and containing less nonfat impurities than older products. In many modern applications, including particularly the manufacture of synthetic surface-active agents, mixed acids are less satisfactory than products which consist predominantly of one or two acids; in many others, absence of appreciable color or taste or odor is essential. There is every indication that this trend will continue, and that the fatty acid industry, once dependent almost entirely upon animal fats, will make increasing use of vegetable oils and such low-priced materials as vegetable oil soapstocks and tall oil.

Among the manufactured products in which fatty acids are used in large quantities are soaps, synthetic surface-active agents, alkyd resins, lubricating greases, rubber tires and other rubber products, candles, cosmetics, polishes and buffing compounds, matches, mold lubricants, and waterproofing and water-repellent compositions.

3. Metal Soaps

There is a considerable manufacture of heavy metal soaps, usually "stearates" or "oleates," which are prepared in most cases by the double decomposition of a sodium or ammonium soap and a solution of a metal salt.

The metal soaps are valuable as metal carriers, and because of their relatively low solubility in water, combined with many of the properties

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[38a] See *Chem. & Eng. News*, **27**, 3592 (1949).

of alkali soaps, including a waxy nature and an ability to form gels with nonaqueous solvents.

The most common metal soaps are aluminum and zinc stearates, each of which was produced in the United States in 1946 to the amount of nearly 9.5 million pounds. Aluminum soap is widely used in the manufacture of lubricating greases, and also in waterproofing compounds. Zinc stearate is used as an internal lubricant for rubber, where it also appears to perform a chemical function in controlling vulcanization. It is a common ingredient of face powders and many cosmetic and pharmaceutical specialties. Recently the zinc soaps of odd-chain fatty acids, e.g., zinc undecanoate, have been found to be effective nontoxic fungicides. There is also a large production (ca. 3.0 million pounds yearly in the United States) of calcium stearate, as well as smaller amounts of soaps of magnesium, barium, copper, mercury, nickel, cobalt, lead, cadmium, and chromium. The heavy metal soaps used as paint dryers are now largely naphthenates and to a lesser degree, resinates or tall oil products, rather than fat derivatives.

4. Other Fatty Acid Derivatives

The dibasic acids, sebacic and azelaic, are produced commercially from fatty oils, the former by the decomposition of castor oil (Chapter II), and the latter by the oxidative fission of commercial oleic acid.

Recently, a number of nitrogen-containing fatty compounds have been made available commercially as chemical intermediates.[38] These include nitriles, marketed under the trade name of Arneels, amines, marketed under the name of Armeens, and their acetate salts (Armacs), and amides, marketed as Armids.

As mentioned previously, a variety of fatty alcohols are available, as well as esters or partial esters of polyhydric alcohols other than glycerol, and esters of both high and low molecular weight monohydric alcohols.

E. Synthetic Fats and Fatty Acids

The manufacture of synthetic fatty acids from hydrocarbons was carried out on a large scale in Germany in the years during and immediately preceding World War II. At the peak of production they were apparently produced at a rate approaching 100,000 tons yearly.

The technology of synthetic fatty acid manufacture has been discussed by a number of writers, including Wittka,[39] from whom the following is taken.

[39] F. Wittka, Soap Sanit. Chemicals, 16, No. 8, 28–32, 73 (1940); see also F. Wittka, Gewinnung der höheren Fettsäuren durch Oxydation der Kohlenwasserstoffe. J. Barth, Leipzig, 1940.

Synthetically prepared paraffins prepared from water gas by the Fischer-Tropsch process are employed as the raw materials. The crude paraffins, consisting of a mixture of members of widely varying molecular weights, are fractionally distilled and the portion comprising paraffins of about 19 to 28 carbon atoms is reserved for further treatment. It is necessary to employ paraffins with hydrocarbon chains approximately twice the length of the fatty acids desired.

The selected paraffin stock is subjected to an oxidizing pretreatment involving mixing with about 0.1% powdered potassium permanganate or other chemical oxidizing agent, heating to about 150°C. for a brief period, and then blowing with air at about 100°C. The pretreatment serves to initiate the formation of peroxides, which must be present for the subsequent stage of oxidation to proceed rapidly.

After pretreatment, the stock is blown with air in towers of special design, with aluminum bodies and alloy heads,[40] until 30 to 50% of the paraffins have been oxidized to form acids. A catalyst consisting of manganese soaps amounting to 0.5 to 1.0% of the weight of the stock is employed. The operation is carried out at a temperature of about 100°C., and requires in the neighborhood of 24 hours. In the course of oxidation, rupture occurs more or less at random along the hydrocarbon chains, hence a mixture of fatty acids of different chain lengths is formed, in addition to a great variety of other decomposition products.

TABLE 99

ANALYSIS OF SYNTHETIC FATTY ACIDS

Solidification point	26.2°C.
Odor	Practically none
Acid value	244.2
Saponification value	247.2
Average molecular weight	229.8
Iodine value	4.9
Hydroxyl value	3.7
Naphtha-insoluble, %	0.0
Unsaponifiable matter, %	0.29

The fatty acids and other acidic substances formed in the oxidized stock are separated from a high proportion of unsaponifiable material by saponifying the mass with sodium carbonate, and discarding the water-insoluble material remaining after saponification. The crude fatty acids obtained by splitting the resulting soaps with a mineral acid are purified by extraction with various solvents, followed by fractional distillation, which serves to select the fatty acids of medium molecular weight which are desired in the final material. For typical products the analysis in

[40] E. L. Baldeschweiler, *Chimie & industrie*, **55**, 329–330 (1946).

Table 99 and the following composition (in per cent by weight) are quoted: C_8, 0.4; C_9, 2.1; C_{10}, 5.0; C_{11}, 7.3; C_{12}, 13.9; C_{13}, 16.3; C_{14}, 15.2; C_{15}, 12.4; C_{16}, 8.1; C_{17}, 7.3; C_{18}, 3.5; C_{19-21}, 7.3; and C_{22}, 1.2.

A more recent method of synthesis forms the basis of the so-called "Oxo" process, which apparently has not yet seen wide-scale use. Although also based on the oxidation and splitting of hydrocarbon chains, the raw material consists predominantly of unsaturated members (olefins), and the immediate oxidation products are aldehydes and ketones, rather than aliphatic acids. It is claimed to produce a material less contaminated with undesirable and difficultly removable impurities than the older process described above.

Although synthetic fatty acids were produced primarily for use in soaps and other detergents, appreciable quantities of a selected fraction were esterified with glycerol or a monohydric alcohol and used in the manufacture of margarine. The following analytical data have been given[41] for a synthetic glyceride product: melting point, 36.5°C.; iodine value, 11; saponification value, 235; odor and flavor, none; keeping time, over 2 years; appearance, like butterfat; composition: C_{11} acids, 18%; C_{12} acids, 18%; C_{13} acids, 20%; C_{14} acids, 8%; C_{16} acids, 15%; C_{10}, C_{18}, C_{19}, and C_{20} acids, 3%; and esters of high boiling point, 11%.

The German synthetic fatty acid program was deeply involved with political considerations, and was propagandized accordingly. Consequently, it has been difficult to give it a proper scientific and economic evaluation. However, the best disinterested opinion appears to be that present methods of synthesis are wholly uneconomic upon any other than an emergency basis, and that there is considerable doubt concerning the acceptability of the synthetic fats as a food product. Although they may be freed of certain impurities, including hydroxy acids, keto acids, dibasic acids, lactones, etc., by suitable processing, there is a considerable content of branched chain acids which is very difficult to remove. There is evidence that some of these are toxic upon long ingestion.[42]

[41] A. Krautwald, *Deut. Gesundheitsw.*, *3*, 354–356 (1948).
[42] See, for example, K. Thomas and G. Weitzel, *Deutsche Med. Wochenzeitschrift*, *71*, 18 (1946).

D. UNIT PROCESSES IN OIL AND FAT TECHNOLOGY

HANDLING, STORAGE, AND GRADING OF OILS AND OIL-BEARING MATERIALS

A. Deterioration in Crude Oils and Oil-Containing Materials

One of the most important branches of oil and fat technology deals with techniques for handling and storing oil-containing materials in such a manner as to minimize deterioration, and with the development of analytical methods that will accurately reflect the extent of any deterioration that has occurred, thus providing a proper measure of the quality as well as the quantity of the contained oil, and hence of its true value as a raw material.

It may be explained that some slight deterioration, at least, is to be expected in any commercial oil-bearing material, and is, in fact, inherent in the processes by which fat is formed. In the living plant or animal, fats, carbohydrates, and proteins are synthesized in a complicated series of steps with the aid of certain organic catalysts or enzymes. These, like other catalysts, are capable of assisting the reverse as well as the forward reactions in question, and hence, under the proper conditions, may promote the degradation of the very substances which they have previously been instrumental in synthesizing.

In living organisms biologists conceive of an "energy pressure" which serves to maintain synthesis predominant. If the organism dies, or if a portion of it is cut off in any way from the living remainder, the inflow of energy essential to synthesis will cease. Then, unless something occurs to render the enzymes inactive, degradation will ensue. Dead tissues, of course, offer no resistance to the growth of microorganisms and, if conditions are favorable, the action of bacteria or fungi usually assumes a dominant role in the process of decomposition.

Enzymes are all heat-labile, being generally inactivated by temperatures of the order of 50–70°C. Their activity may be inhibited chemically, and they exhibit maximum activity only within certain optimum ranges of pH. Even in materials of relatively low moisture content, they operate actually in an aqueous substrate; hence dehydration reduces their effectiveness.

The degradation of proteins, carbohydrates, phosphatides, etc., in fatty tissues serves to produce oil-soluble substances from non-oil-soluble

precursors, and hence tends to contaminate the oil or fat with impurities which would not normally be present, and which are often dark colored and objectionable in odor and flavor. In addition, the process of deterioration is invariably accompanied by a certain amount of fat splitting, with the production of free fatty acids in the oil. These are generally undesirable constituents which must be removed by subsequent refining and the assumption, on the part of the oil processor, of a refining loss. Hence, in addition to its influence upon oil quality, the amount of deterioration has a direct bearing upon the yield of usable oil from a given material.

If the crude oils expressed from oily tissues contain moisture, and if they have not been heated sufficiently for the inactivation of enzymes, similar degradation and deterioration can, of course, continue. Generally, however, expression of the oil is preceded by heat treatment, and the changes in storage with which the oil processor is concerned are not associated with enzyme action and are not largely productive of free fatty acids, but are chemical changes, probably associated with oxidation, which reduce the stability of the oil and make it difficult to bleach to an acceptable light color.

1. FATTY ANIMAL TISSUES

The fats in living animal tissue are said to be virtually devoid of free fatty acids, hence the appreciable acidity of commercial animal fats can be ascribed purely to enzyme action.[1] The visceral fatty tissue of an animal is invariably more subject to fat lipolysis than other fatty tissues of the same animal (Fig. 62).

Usually, animal fats are rendered within a few hours after the animals are killed. The principal exceptions are salt lard and other lards derived from cured pork cuts, and certain inedible tallows and greases, all of which are low-grade products. In the latter, decomposition of the material may be far advanced from bacterial action. Edible animal fats, such as lard and oleo oil, are not usually refined for reduction of their free fatty acid content; consequently it is particularly important for rendering to be conducted promptly, before the free acids have become excessively high. Since the enzymes responsible for fat splitting are quickly inactivated by moderately elevated temperatures, it is good practice to charge the fatty stock to the rendering apparatus as quickly as it is available. The application of heat will arrest hydrolysis, even though the actual rendering operation may be somewhat delayed. Excessive enzyme action may also be avoided by refrigerating fatty stocks if it is unavoidable that some time must elapse before they are rendered, but it is difficult to chill the stock quickly, and appreciable lipolysis will continue even at

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[1] D. Fairbairn, *J. Biol. Chem.*, *157*, 645–650 (1945).

reduced temperatures; hence in general the expedient of heating is to be preferred.

It is possible to produce animal fats with a free fatty acid content of 0.15% or less from very fresh stock. However, oleo oil and lard usually contain 0.2 to 0.5% of free acid. Edible tallow often contains 0.5 to 1.5% of free acids, and inedible tallows and greases may run as high as 40 or 50% in free fatty acids.

Marine oils are also usually rendered from fairly fresh stock. It is particularly injurious to the quality of the oil to allow fish to deteriorate before they are processed, because of the powerful proteolytic enzymes present in this class of material. Fish oil in contact with decomposing proteins absorbs appreciable quantities of nitrogenous compounds which appear to enter actually into chemical combination with the oil.[2] Combined nitrogen in the oil contributes greatly to undesirable color, flavor, and odor.

2. Oil-Bearing Fruits

The high moisture content of palm fruits and olives, like that of animal tissues, is favorable to enzyme action; hence these materials must be processed promptly if they are to yield oil of low free fatty acid content. Palm fruits are particularly susceptible to deterioration. Their lipolytic enzymes are so active that even under the most favorable conditions palm oil is seldom produced with a free fatty acid content of less than 2 or 3%, and under crude conditions of processing the free acid content of this oil may be as high as 20, 40, or even 60% or more. According to Barnes,[3] the lipolytic enzyme of palm fruit is destroyed by a temperature of 55°C. Enzyme action is slow in freshly cut, undamaged bunches of fruit, but becomes extremely rapid if the fruits are bruised. It is virtualy impossible to harvest the fruit bunches without some slight damage. According to the best practice,[4] all fruit bunches are "sterilized" by exposure to open steam as soon as possible after harvesting. The sterilization treatment serves the dual purpose of inactivating the enzymes and loosening the fruits to permit threshing from the stalks. Olives are less liable to lipolytic action. They are more or less bruised in harvesting and are often stored for days before they are processed, but such treatment is detrimental to the quality of the oil, which in Europe seldom contains less than 1% free fatty acids, and may run as high as 5% or more.

[2] W. L. Davies and E. Gill. *J. Soc. Chem. Ind.,* **55**, 141–146T (1936).
[3] A. C. Barnes. "Chemical Investigations into the Products of the Oil Palm." Nigeria Dept. Agr. *Special Bull.* (1924).
[4] B. Bunting. C. D. V. Georgi, and J. N. Milsum. *The Oil Palm in Malaya,* Dept. Agr., Straits Settlements and Federated Malay States, Kuala Lumpur, 1934.

3. Oilseeds

While oil-bearing seeds are much less subject to damage than the materials of high moisture content mentioned above, and are capable of being stored for long periods under suitable conditions, they are nevertheless a perishable commodity, and their large-scale storage and handling often present a considerable problem.

It may be pointed out that the function of the seed in the life cycle of the plant is in itself a guarantee of intense biological activity accompanied by degradative processes, once the seed is given access to moisture at the proper temperature. The constituents of the seed that make it a useful industrial raw material—proteins, carbohydrates, and fat—are the reserves that are provided to nourish the seedling plant, and the organic makeup of the seed is naturally such as to render these reserves readily available when they are needed.

In one respect, deterioration in oil seeds is fundamentally different from that in fatty animal tissues. Whereas the fat in the latter is substantially neutral when the animal is killed, the oil in oil seeds may have already undergone considerable hydrolysis by the time the seeds are mature and ready for harvesting. Normally, as the seeds gradually mature and become detached from the plant, and as the "energy pressure" responsible for maintaining synthesis and preventing degradation lessens, there is a concurrent dehydration of the seed, which inhibits enzyme or other biological activity. This suppresses splitting of the oil, but by no means perfectly, so that even under the most favorable conditions oil in mature seed contains an appreciable amount (usually about 0.5%) of free fatty acids. If the seeds become artificially wetted during the period mentioned, or suffer damage mechanically or from frost, the acidity of the oil may be much greater.

(a) Effects Accompanying Deterioration

Two readily observable effects accompany and roughly parallel deterioration of the oil in stored oil seeds. One of these is respiration, or the generation and evolution of carbon dioxide through atmospheric oxidation of constituents of the seed. The respiration intensity of sound seeds of low moisture content is usually less than 0.1 cc. of carbon dioxide per gram of seed per day, but in damaged seeds of high moisture content it may rise to 5.0 cc. or more. The *respiratory quotient*, defined as the ratio of carbon dioxide evolved to oxygen absorbed, is an indication of the class of substances undergoing oxidation. In aerobic respiration it is theoretically unity if the latter consist of carbohydrates, but less than unity if they are proteins or fats, which are less rich in oxygen.

The other effect is a generation of heat, which is an unfortunate concomitant, inasmuch as it tends to raise the temperature of a large seed mass, and thus intensify deterioration. Cases have been recorded of heating so severe as to char the seed.

Many of the experimental storage studies of deterioration have been concerned with respiration or heating rather than the less easily measured factor of oil deterioration *per se.*

(b) *Relative Roles of Seed Enzymes and Microorganisms*

Since conditions leading to intensive enzyme action are equally favorable to the growth of bacteria and molds, and since the two produce similar deterioration in stored oil seeds, it is not easy to assign to each its proper role. Of the three groups of workers who have recently given the problem intensive study, Altschul and co-workers,[5] working with cottonseed, have expressed the conviction that in seed with a moisture content up to 14–15%, native enzymes of the seed are primarily responsible for deterioration, although at higher moisture contents they admit the probability of the activity of microorganisms being an important or even a dominant factor. Their opinion is based in part on experiments on the chemical inhibition of deterioration in which it was found that treatment that retarded lipolysis might even stimulate respiration. If deterioration were the result of biological activity within the seed, it is conceivable that some manifestations might be more susceptible to inhibition than others, whereas simple repression of mold and bacterial growth should affect lipolysis and respiration alike. On the other hand, Geddes and co-workers,[6] on the basis of experience with soybeans, and Larmour, Sallans, *et al.,*[7,8] from similar experience with flaxseed, have attributed deterioration at the lower moisture levels to mold growth, and considered enzyme action a probably important factor only when the moisture content becomes relatively high, *i.e.,* approaching that required for germination. This viewpoint is supported by the observation that heating and respiratory activity increase sharply at a moisture content that is critical for each seed, and that this moisture content corresponds to hygroscopic equilibrium at the relative humidity (74–75%) at which the most xerophytic species of common mold (*Aspergillus glaucus*) begins to thrive.

[5] See A. M. Altschul, Chapter V, in *Cottonseed and Cottonseed Products,* A. E. Bailey, ed., Interscience, New York, 1948.

[6] See M. Milner, Chapter XIII, in *Soybeans and Soybean Products,* K. S. Markley, ed., Interscience, New York, 1950.

[7] R. K. Larmour, H. R. Sallans, and B. M. Craig, *Can. J. Research, F22,* 1–18 (1944).

[8] H. R. Sallans, G. D. Sinclair, and R. K. Larmour, *Can. J. Research, F22,* 181–190 (1944).

(c) Effect on Seed Composition and Oil Quality

The effect of deterioration and heating on the chemical composition of cottonseed was investigated by Malowan.[9] Neither oil nor protein was found to be consumed in the course of heating which appears to be a process fueled purely by the combustion of carbohydrates. However, there was considerable degradation of proteins, as indicated by an increase in "magnesia nitrogen" consisting of ammonia and other loosely bound nitrogen, plus, of course, extensive hydrolysis of the oil. More or less similar changes have been observed in soybeans[10-13] and peanuts[14] stored at high moisture contents. In these again, there is no significant loss of oil or total nitrogen, but denaturation of proteins takes place, and there is a marked decrease in nonreducing sugars and a corresponding increase in reducing sugars. In a series of experiments with normal soybeans stored for one year at moisture contents up to 20.9% there was no increase in the amount of nonprotein nitrogen,[10] but in field-damaged beans a large increase was observed.[11] The oil in normal beans stored at a moisture content of 17.1% or more was observed to decrease 25–40 units in iodine value.[10]

While the effect of seed deterioration on the contained oil is evidenced most obviously in hydrolysis to produce a high content of free fatty acids, this is by no means the only undesirable result. Degradation of the non-glyceride constituents of the seed invariably produces pigmented oil-soluble materials which make the oil dark and difficult to bleach, and usually also make the color of the oil unstable after bleaching. In addition, the stability of the oil suffers, particularly if it is an oil such as soybean oil, which is naturally poor in flavor stability.[15] Increase in the diene conjugation of the oil has been observed[16] in both cottonseed and peanuts subjected to long storage.

In addition to its effect on oil quality, it is generally observed that extensive deterioration makes the mechanical processing of oil seeds difficult. It also leads to a low oil recovery, even if no oil is actually destroyed.

[9] J. Malowan, *Cotton Oil Press*, 5, No. 4, 40–43 (1921).
[10] P. E. Ramstad and W. F. Geddes, *Minn. Agr. Expt. Sta. Tech. Bull.*, No. 156 (1942).
[11] M. Milner, B. Warshowsky, I. W. Tervet, and W. F. Geddes, *Oil & Soap*, 20, 265–268 (1943).
[12] M. Milner and W. F. Geddes, *Cereal Chem.*, 23, 449–470 (1946).
[13] O. A. Krober and F. I. Collins, *J. Am. Oil Chem. Soc.*, 25, 296–298 (1948).
[14] M. F. Stansbury and J. D. Guthrie, *J. Agr. Research*, 75, 49–61 (1947).
[15] See J. H. Sanders, *Oil & Soap*, 21, 357–360 (1944).
[16] W. A. Pons, Jr., M. D. Murray, R. T. O'Connor, and J. D. Guthrie, *J. Am. Oil Chem. Soc.*, 25, 308–313 (1948).

(d) Influence of Moisture Content

Since there are more or less critical moisture levels for the proliferation of both molds and bacteria, and since enzymes likewise function in an aqueous substrate, it is not surprising that the moisture content is the most important factor in determining the ability of oil seeds to store well.

Although forced seed dryers are often a part of modern storage facilities, it is much more common for oil seeds to be air-dried, in which case their eventual moisture content is determined by the relative humidity of the atmosphere. Many experimental investigations have been concerned with the hygroscopic equilibrium of different seeds, of which there may be mentioned the work of Franco,[17] Simpson and Miller,[18] and Karon and Adams[19] on cottonseed; of Larmour, Sallans, and Craig[7] on soybeans, flaxseed, and sunflowerseed; of Coleman and Fellows[20] on flaxseed; of Ramstad and Geddes[10] and Beckel and Cartter[21] on soybeans; and Karon and Hillery[22] on peanuts.

As the moisture content of the nonoil portion of the seed rather than the whole seed is the important factor in oil seed deterioration, the so-called "critical moisture level" for the beginning of rapid spoilage is relatively high for seeds of low oil content, and relatively low for high-oil seeds. In carefully controlled laboratory experiments with sound and well-cleaned seeds it has been noted that at 25°C. the critical moisture content for high respiratory activity is between 11.8 and 12.8% for whole flaxseed, between 9.9 and 10.8% for whole sunflowerseed, and between 7.0 and 8.5% for decorticated sunflowerseed.[7] The corresponding moisture level for a sample of soybeans was found to lie within the narrow range of 14.0–14.6%.[23]

Because the presence of trash or damaged seed increases susceptibility toward deterioration, and because heating has been observed at moisture contents slightly below those required for high respiration rates,[8] the accepted moisture levels for safe commercial storage are a little below those quoted above, e.g., about 10.5% for flaxseed, 9.5% for sunflowerseed, and 13.0% for soybeans. The moisture limit for the safe storage of copra is about 6.0%,[24,25] and for palm kernels about 8.0%.[4]

[17] C. M. Franco, Bragantia. 3, 137–149 (1943).
[18] D. M. Simpson and P. R. Miller. J. Am. Soc. Agron., 36, 957–959 (1944).
[19] M. L. Karon. J. Am. Oil Chem. Soc., 24, 56–58 (1947). M. L. Karon and M. E. Adams, ibid., 25, 21–22 (1948).
[20] D. A. Coleman and H. C. Fellows. Cereal Chem., 2, 275–287 (1925).
[21] A. C. Beckel and J. L. Cartter, Cereal Chem., 20, 362–368 (1943).
[22] M. L. Karon and B. E. Hillery, J. Am. Oil Chem. Soc., 26, 16–19 (1949).
[23] M. Milner and W. F. Geddes, Cereal Chem., 23, 225–247 (1946).
[24] F. C. Cooke, Malayan Agr. J., 19, 128–136 (1931).
[25] F. S. Ward, Dept. Agr., Straits Settlements and Federated Malayan States Sci. Ser., No. 20, 95–108 (1937).

Sallans and co-workers[8] have made the important observation that for a number of oil seeds the so-called critical moisture content corresponds very closely to that at which the seeds are in equilibrium with air of 74–75% relative humidity. This humidity, in turn, is that at which species of molds known to contribute to deterioration begin to proliferate. Hence it seems probable that the critical factor in the deterioration of many seeds is not the moisture content of the seed *per se*, but the humidity of the interstitial air in the storage bins. This point of view has been further developed by Milner and Geddes.[23]

It may be mentioned that mold growth may be far enough advanced to affect the seeds markedly without being visible to the naked eye.[7]

Presumably because of the greater degree to which enzyme activity contributes to deterioration, cottonseed exhibits a more complicated reaction to moisture content in storage. Respiration studies[26] indicate no sharp break at any particular moisture content, but rather a smooth exponential relationship between the moisture content and an "average respiration intensity" over a period of 100 days or more. At a moisture content of about 12–13%, the respiration rate was found to be similar to that observed previously by Larmour *et al.*[7] for flaxseed and sunflowerseed. A similar exponential relationship is observed[26a] between moisture content and the rate of hydrolysis of the contained oil.

According to Robertson and Campbell,[27] cottonseed with a moisture content below 10% can generally be depended upon to keep well in commercial storage, and seeds with moisture above 14% will generally deteriorate considerably, whereas those within the range of 10–14% will be found to be variable in behavior. In practice, the temperature, the initial quality of the seeds, their previous history, the type of storage facilities, and the contemplated length of storage are all important factors in determining the keeping properties at any specific moisture level.[28]

It may be noted here that seasonal temperature variations may cause a movement of air in oil seed storage bins that will transfer moisture from warm to cold portions of the seed mass, and thus produce pockets of high moisture content even in seeds that have been stored at a safe moisture level. Thus, for example, Carter and Farrar[29] found that soybeans stored in a tight bin in the fall at a moisture content of 12% transmitted suffi-

[26] M. L. Karon and A. M. Altschul, *Plant Physiol.*, *21*, 506–521 (1946).
[26a] L. Kyame and A. M. Altschul, *Plant Physiol.*, *21*, 550–561 (1946).
[27] F. R. Robertson and J. G. Campbell, *Oil & Soap, 10*, 146–147 (1933).
[28] For a complete discussion of moisture content in relation to cottonseed storage, and other aspects of cottonseed storage and handling, see O. H. Alderks, Chapter XIII, in *Cottonseed and Cottonseed Products*, A. E. Bailey, ed., Interscience, New York, 1948.
[29] D. G. Carter and M. D. Farrar, *Agr. Engr., 24*, 296 (1943).

cient water vapor to upper portions of the bin to increase the moisture content to 16–19%. It has been stated[30] that in commercial storage the migration of moisture does not affect enough soybeans to present a serious problem unless the original moisture content is above about 13%.

Localized heating in seed storage bins will produce a similar movement of air, which may also cause moisture to be transferred from one zone to another.[10,31]

(e) *Influence of Temperature*

In the case of soybeans and similar oil seeds, where deterioration appears to be primarily a result of the growth of microflora, the storage temperature does not appear to be a major factor and has been generally neglected in the storage investigations reported to date. However, it is recognized as a highly important factor in the storage of cottonseed. The respiration of cottonseed is markedly temperature-dependent,[9] and the effect of even small increases in temperature on the rate of deterioration is recognized by all mill operators.[28] It is because of the undesirable effect of high temperatures that most seed houses are equipped with aeration ducts and large ventilating blowers to cool the seed during the winter months and to dissipate the heat from pockets that show a tendency to undergo rapid deterioration. The insulating effect of the adherent linters on cottonseed contributes to the peculiar tendency of this seed to heat in storage.

Since high temperatures will not only destroy microorganisms, but also inactivate enzymes, it might be expected that the heating of deteriorating seed would not be autocatalytic to an unlimited extent, but that a temperature would eventually be reached at which further deterioration would be inhibited. Such an effect has actually been observed in laboratory experiments with flaxseed and sunflowerseed,[8] with the temperature leveling off at 50–55°C., corresponding to the thermal death point for common molds. However, temperatures much higher may be produced, from the action of thermophilic bacteria, or from oxidation uncomplicated by biological factors. Ramstad and Geddes[10] recorded temperatures as high as 80°C. (176°F.) in laboratory experiments with soybeans, and Altschul[5] mentions temperatures as high as 190°F. in commercially stored cottonseed. In fact, cases of spontaneous combustion in cottonseed are known. In general, deterioration is so far advanced by the time enzymes, molds, and bacteria are inactivated that their inactivation by heating is of little practical significance.

[30] L. E. Holman, Chapter XII, in *Soybeans and Soybean Products*, K. S. Markley, ed., Interscience, New York, 1950.
[31] M. Milner and W. F. Geddes, *Cereal Chem.*, 22, 477–483 (1945).

(f) Influence of Miscellaneous Factors

The deterioration of oil seeds, through enzyme action or infestation by microorganisms, is greatly stimulated by mechanical damage to the seed cells; the latter may occur during handling or processing operations that break or crush the seed, or from exposure of the seed to the weather. Because of this, undecorticated seed always keep better than decorticated seed, and deterioration is rapid after the seed have been ground or rolled in preparation for expression of the oil. In the processing of oil seeds which must necessarily be decorticated at the point of origin, such as copra and palm kernels, there is always a certain quantity of "fines" produced. The oil in this material invariably becomes high in free fatty acids. A clean cut or fracture in a large oil seed causes much less damage than crushing of edges or corners to produce "fines." Oil seed "splits" do not necessarily deteriorate rapidly or yield an inferior oil.

Since heating and deterioration is essentially an aerobic process, it may be inhibited by maintaining the seed in an atmosphere low in oxygen. Laboratory experiments have been carried out in which the interstitial air in cottonseed was replaced by hydrogen,[32] and in which soybeans were stored in nitrogen and under a vacuum.[33] The carbon dioxide evolved by respiring seeds appears to have some retarding influence on deterioration, as in laboratory experiments the respiration rate is considerably influenced by the rate of aeration of the sample.[10]

Immature seeds, harvested before their enzymes have become dormant, deteriorate more readily than normal seeds.

(g) Relation to Previous History of the Seed

Degradative processes in seeds increase the supply of nutrients for the growth of microflora and stimulate enzyme activity; hence deterioration is autocatalytic. In any lot of seeds, therefore, the keeping properties depend largely upon the extent to which deterioration has proceeded before the seed are put into storage.

Damage to the seed, leading to poor storage characteristics, occurs when the mature seeds are allowed to stand for a prolonged period in the fields before they are harvested, particularly if this is a period of heavy rainfall and also when early frosts arrest growth before the seeds are mature. In the southern United States seasons of excessive rainfall during harvesting, e.g., 1937–38, are always marked by poor seed quality, and regions of relatively heavy rainfall, e.g., Louisiana and southern Mississippi, consistently produce seed with oil of relatively high acidity. In the soybean-producing sections of the United States an early frost in the fall of 1942,

[32] J. Malowan, Cotton Oil Press, 4, No. 11, 47–49 (1921)
[33] A. Guillaumin, Compt. rend., 187, 571–572 (1928).

followed by overloading of handling and storage facilities and slow harvesting, resulted in unprecedented field damage. The peculiar problems created by these conditions have been discussed by Freyer[34] and others.

In addition to the more or less obvious effect of prior deterioration accompanied by lipolysis on the quality and storage characteristics of oil seeds, there is ample evidence that, in cottonseed, at least, there may be invisible changes prior to harvesting which will markedly affect the subsequent behavior of the seed. In other words, different lots of seed of equally low initial acidity and moisture content may exhibit very different rates of deterioration in storage. Meloy,[35] who has studied this effect extensively, has advanced the hypothesis that atmospheric humidity during the period that the seeds mature and dry is the principal factor in determining their subsequent storage properties. Apparently, seeds matured at a low humidity tend to be stable even if they are later exposed to rain, whereas seeds matured at a high humidity tend to deteriorate even if later dried to a low moisture content. The instability of the seeds maturing in a humid atmosphere is attributed to a retention of enzyme activity during a period when the enzymes would normally become dormant. As pointed out later by Altschul,[5] this could be expected to leave the enzymes in a condition favorable to resumed activity at a later date.

The critical period in the maturation of cottonseed appears to be within 10–15 days after opening of the bolls, when, under ideal weather conditions, the moisture content of the seed decreases from about 50 to 10%.

(h) Beneficial Effect of Storage

Not all changes occurring in stored oil seeds are undesirable. The yield of oil from newly harvested soybeans is less than from the same beans after a period of storage.[36] The storage of soybeans also results in a diminution in the chlorophyll content of "green beans." Chlorophyll in the oil is undesirable because of the difficulty of removing green color in subsequent processing, and because of the tendency of the color to become intensified by hydrogenation.

4. Kinetics of Lipolysis

As mentioned previously, the splitting of neutral fat in stored oil seeds is an autocatalytic process, in which the rate increases progressively as

[34] E. Freyer, *Oil & Soap, 22,* 13–22 (1945).
[35] G. S. Meloy, *Oil & Soap, 16,* 174–178 (1944); Address, 48th Annual Meeting, National Cottonseed Products Association, New Orleans, May 17–18, 1944.
[36] K. S. Markley and W. H. Goss, *Soybean Chemistry and Technology.* Chemical Pub. Co., New York, 1944.
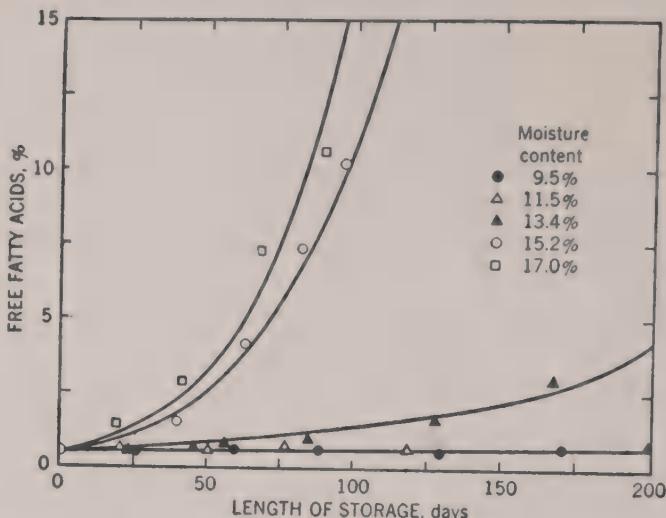
Fig. 61. Free fatty acids content of oil in cottonseed of various moisture contents *vs.* storage time of the seed.[37]
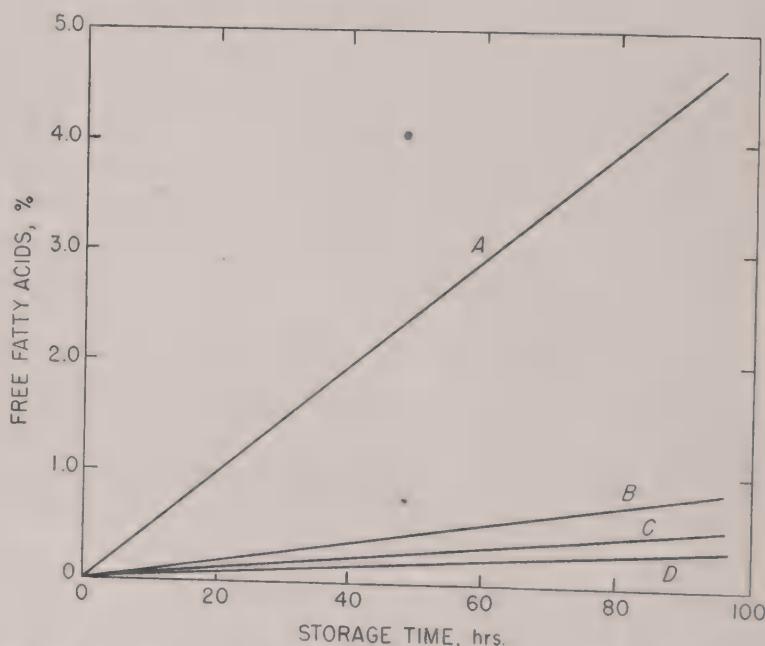
Fig. 62. Development of free fatty acids in: (*A*) ruffle fat, (*B*) leaf fat, (*C*) caul fat, and (*D*) back fat stored at 34°F.[37a]

the storage time is extended. Karon and Altschul[37] found that in cotton-seed the progress of lipolysis could be represented quantitatively by the differential equation:

$$dF/dt = kF (100 - F)$$

[37] M. L. Karon and A. M. Altschul, *Plant Physiol.*, *19*, 310–325 (1944).

where t = time, F = percentage of free fatty acids, and k = a rate constant which is dependent upon the storage temperature and inherent storage stability of each seed sample. Hence, a plot of free fatty acids content of the oil against storage time yields an exponential curve (Fig. 61).

On the other hand, it has been shown[37a] that in stored animal tissues there is simply a linear relationship between the acidity of the fat and the storage time (Fig. 62).

5. DETERIORATION IN STORED OILS

Very prolonged storage of any fatty oil is undesirable because of the deterioration that occurs through oxidation. Because of this, lard or other animal fats lacking in natural antioxidants are generally put into refrigerated storage if they must be held for long periods. However, vegetable oils may generally be stored in large tanks (with limited access to air) for considerable periods without serious detriment to their stability.

Of rather more concern than any decrease in their stability toward oxidation are changes which impair the color or color stability of stored vegetable oils. In the case of cottonseed oil these occur more readily in crude than in refined oils; hence this oil is usually stored in the refined rather than the crude form. Comparative storage data on crude and refined oils have been recorded by King.[38] In one instance, crude cottonseed oil of good quality and a free fatty acids content of 0.7% showed no increase in acidity during approximately 5 months of commercial storage (January to May), and only a negligible increase in refining loss (5.0 to 5.3%), but the refined oil color increased from 4.7 to 5.6 Lovibond red units, and the bleach color increased from 0.9 to 1.9 units.[39] On the other hand, a large tank of refined oil exhibited no increase in acidity during approximately 6 months of storage from February to August, and in this period the refined oil color decreased from 7.0 to 6.3 red, and the bleach color decreased from 2.5 to 1.9 red. An improvement in the bleachability of refined cottonseed oil upon storage is quite commonly, though not invariably, observed. It will be seen that storage of the crude oil affected the bleach color more than the refined oil color.

The color reversion of crude cottonseed oil has been studied by Williams and co-workers.[40] It is apparently related to oxidation in the complex

[37a] F. C. Vibrans, *J. Am. Oil Chem. Soc.*, **26**, 575–580 (1949).
[38] R. R. King, *Oil & Soap*, **18**, 16–21 (1941).
[39] The term "refined oil color" refers to the color of the oil refined in the laboratory according to the official methods of the National Cottonseed Products Association and the American Oil Chemists' Society; the term "bleach color" refers to the color of the refined oil after bleaching by the official method.
[40] P. A. Williams, C. H. Boatner, C. M. Hall, R. T. O'Connor, and L. E. Castillon, *J. Am. Oil Chem. Soc.*, **24**, 362–369 (1947). P. A. Williams, R. P. Hadden, C. M. Hall, L. E. Castillon, W. A. Guice, R. T. O'Connor, and C. H. Boatner, *ibid.*, **26**, 28–34 (1949).

pigment system of the oil; the production of oils with marked reversion properties is favored by a low moisture content in the cottonseed meats during cooking; hence expeller or screw-pressed oils tend to revert more than hydraulic pressed oils. However, a tendency toward color reversion is inherent in certain lots of seed, and reversion will take place upon storage of either the seed or the expressed oil.

Since, as indicated above, the bleach color is affected more adversely than the refined oil color, in strongly reverting oils the normal relationship between these colors does not hold; reverting oils also were observed to have a high ultraviolet and near ultraviolet absorption, in the range of 320–420 mμ. Crude oil from so-called "bollie" or immature seed is extremely unstable in color; a case has been reported by Fash[41] in which the refined oil color increased from 4.8 to 10.9 red in 30 days. Admixture of bollie oil with normal oil appeared to affect adversely the color stability of the latter.

It may be mentioned that the color of "reverting" oils tends to be unstable and to increase readily with slight oxidation even after the oil has been bleached, hydrogenated, deodorized, etc.

Soybean oil, because of its very different pigment system, does not normally revert in color, and is commonly stored as crude. It is generally considered that storage in the crude form leads to lower bleach colors than storage in the refined form.

In the case of any oil stored in the crude form it is important for the oil to be clean and, insofar as is possible, free of "foots" or residue of meal from the pressing operation, as this material retains sufficient moisture to promote hydrolysis of the oil in contact with it. Meal settlings are easily reprocessed at the oil mills, but are a source of trouble and oil loss at the refinery. Oils such as undegummed soybean oil which are high in phosphatides invariably deposit a troublesome layer of gummy material upon long standing in storage tanks, or even during the course of long shipments in tank cars.

B. Grading and Evaluation. Trading Rules

1. Evaluation of Oil Seeds

More or less elaborate grading systems have been developed in the United States for determining the value of the major oil seeds. These systems may be divided into two categories: (a) those which aim at establishing the general quality of the seeds, upon the basis of their soundness, their moisture content, and their freedom from foreign matter; and (b) those which are intended to evaluate the oil seeds more exactly, on the basis of the yield and quality of the oil obtainable from them. Obviously

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[41] R. H. Fash, *Oil & Soap*, **11**, 106 (1934).

the latter method of grading and valuation is the more rational, but it requires a chemical analysis of all seed samples and hence is not practicable in all cases.

Under the provisions of the United States Grain Standards Act, all soybeans and flaxseed sold by grade in interstate or foreign commerce must be graded by licensed inspectors in conformity with established standards. The present standards[42] applicable to these two seeds are listed in

TABLE 100

GRADE REQUIREMENTS FOR YELLOW SOYBEANS, GREEN SOYBEANS, BROWN SOYBEANS, BLACK SOYBEANS, AND MIXED SOYBEANS

Grade No.	Minimum test weight per bushel, lbs.	Maximum limits of			
		Moisture, %	Splits, %	Damaged kernels (soybeans and other grains), %	Foreign material, %
1[a]	56	13	10	2	2
2[a]	54	14	20	3	3
3	52	16	30	5	4
4[b]	49	18	40	8	6
Sample grade	Sample grade shall be soybeans which do not meet the requirements for any of the grades from No. 1 to No. 4, inclusive or which are musty, or sour, or heating; or which have any commercially objectionable foreign odor; or which contain stones; or which are otherwise of distinctly low quality.				

[a] The soybeans in grade No. 1 of the class Yellow Soybeans may not contain more than 1.0%, in grade No. 2 not more than 2.0%, and in grade No. 3 not more than 5.0% of Green, Black, Brown, or bicolored soybeans, either singly or in any combination.

[b] Soybeans which are materially weathered shall not be graded higher than No. 4. *Handbook of Official Grain Standards of the United States,* Washington, 1950.

TABLE 101

GRADE REQUIREMENTS FOR FLAXSEED

Grade No.	Minimum test weight per bushel, lbs.	Maximum limits of damaged flaxseed, %
1	49	20
2	47	30
Sample grade	Shall include flaxseed which does not come within the requirements of either of Grades No. 1 or No. 2; or which contains fire-damaged flaxseed; or which contains more than 11% of moisture; or which is musty, or sour, or heating, or hot; or which has any commercially objectionable foreign odor; or which is otherwise of distinctly low quality.	

Tables 100 and 101. Admittedly, trading in oil seeds on the basis of grain standards leaves much to be desired, as the oil content is quite variable, and, in flaxseed particularly, there are large variations in the quality

[42] U. S. Department of Agriculture, Production and Marketing Administration, *Handbook of Official Grain Standards of the United States,* Washington, 1950.

(iodine value) of the oil. Official methods for the analysis of soybeans, which are sometimes used in supplemental trading on the basis of oil content, are provided by the American Oil Chemists' Society[43] and the National Soybean Processors Association.[44]

The trading rules of the National Cottonseed Products Association[45] provide a complete system for grading cottonseed upon the basis of their composition, and also specify methods of analysis for cottonseed and peanuts, and standard formulas for the calculation of oil and of oil cake yields.

Under the present (1950) N.C.P.A. rules, a "Quantity Index" for cottonseed is established as follows:

(a) For cottonseed that by analysis contain 16.5% or more of oil, the Quantity Index shall equal 4 times the percentage of oil, plus 6 times the percentage of ammonia, plus 5.

(b) For cottonseed that by analysis contain less than 16.5% of oil, the Quantity Index shall equal 6 times the percentage of oil, plus 6 times the percentage of ammonia, minus 28.

A "Quality Index" is also established. Seed which contain not more than 1% foreign matter, not more than 12% moisture, and not more than 1.8% free acids in the oil are designated as prime quality seed and have a Quality Index of 100. In the case of cottonseed which fail to meet the requirements for a Quality Index of 100, the Quality Index is reduced below 100 according to the following scheme: (a) 0.4 unit is deducted for each 0.1% free fatty acid in excess of 1.8%; (b) 1.0 unit is deducted for each 1.0% of foreign matter in excess of 1.0%; and (c) 1.0 unit is deducted for each 1.0% of moisture in excess of 12%. A numerical grade (to the nearest 0.5 unit) is then assigned to the cottonseed according to the following equation:

$$\text{Grade} = \frac{(\text{Quality Index})(\text{Quantity Index})}{100}$$

The calculation of grade may be illustrated as follows:[42]

Analysis of the seed:

Oil...	19.0%
Ammonia..	3.84%
Moisture..	13.5%
Free acids......................................	2.4%
Foreign matter.................................	3.0%

[43] American Oil Chemists' Society, *Official and Tentative Methods*, 2nd ed., V. C. Mehlenbacher, ed., 1946 (revised annually).
[44] National Soybean Processors Association, *Yearbook and Trading Rules, 1949–1950*, Chicago, 1949 (issued annually).
[45] National Cottonseed Products Association, *Rules Governing Transactions Between Members, 1949–1950*, Memphis, 1949 (issued annually)

Calculation of the Quantity Index:

$$(4) (19.0) = 76.00$$
$$(6) (3.84) = 23.04$$
$$\text{Plus} \qquad 5.00$$
$$\text{QUANTITY INDEX} = 104.04$$

Calculation of the Quality Index:

Reduction for free fatty acids in excess of 1.8%:
$$(6) (0.4) = 2.4 \text{ units}$$

Reduction for moisture in excess of 12.0%:
$$(1) (1.5) = 1.5 \text{ units}$$

Reduction for foreign matter in excess of 1.0%:
$$(2) (1.0) = 2.0 \text{ units}$$

Total reduction $= 5.9$ units
QUALITY INDEX $= 100$ minus $5.9 = 94.1$

Calculation of the grade:

$$\frac{(104.04) \quad (94.1)}{100} = 97.90 = \text{Grade } 98.0$$

Cottonseed are quoted and sold on the basis grade of 100, with premiums or penalties being assessed for deviations above or below this figure. In calculating the settlement price of the seed, the weight of each shipment is also determined on the basis of the analysis, being adjusted downward in proportion to the amount of foreign matter in the seed, where the content of foreign matter exceeds 1%. Grade premiums or penalties are calculated on the basis of the weight so adjusted. The present N.C.P.A. rules are the product of a long period of evolution characterized by intensive study of analytical methods and the relationship of analytical data to the actual value of the seed to the processor.[45a]

Peanuts diverted to oil crushing in the United States are graded according to U. S. Government standards based upon the percentages by weight of sound and damaged kernels in the unshelled stock, and prices are adjusted, as with cottonseed, according to the oil and protein content, following official methods of the American Oil Chemists' Society.[43]

There are no generally recognized standards or trading rules for imported oil seeds such as copra, palm kernels, sesame seed, etc.

2. OILCAKE AND MEAL

The value of oilcake is dependent primarily upon its protein content, which is customarily reported in terms of ammonia (NH_3), and calculated to protein, using the factor 6.25 in converting from nitrogen to protein. Cottonseed or peanut cake or meal is commonly adjusted to a

[45a] See G. S. Meloy, Chapter X, in *Cottonseed and Cottonseed Products*, A. E. Bailey, ed., Interscience, New York, 1948.

definite protein content at the mill by varying the completeness with which the hulls are separated from the meats or by adding ground hulls to the meal. Cottonseed cake most commonly has a protein content of 41%, or an ammonia content of 8%, although 36% and 43% protein grades are also sold; peanut meal usually is sold as containing 45% protein or 8.76% ammonia. Soybean cake or meal is usually adjusted to a specific protein content by the addition of moisture to the residue coming from screw press or solvent extractor. The standard grades have a moisture content not in excess of 12.5%; the protein content is a minimum of 41% for meal from mechanical expression and 44% for that from solvent extraction.[43]

3. Estimation of Mill Yields

As a convenience to the oil miller, the trading rules of the National Cottonseed Products Association[45] specify methods for calculating reasonable yields of oil and cake of specified protein content from cottonseed and peanuts according to the analyses of the latter.

According to the N.C.P.A. formula for the calculation of yields, the ammonia available in cottonseed for the production of oilcake is considered to be 94% of the ammonia present in the whole seed. The remaining 6% is lost in the hulls and in the dust, etc., incidental to milling operations. The possible yield of oilcake of a definite ammonia content, from a ton of cottonseed is calculated from the ammonia content of the seed and the availability factor of 0.94 referred to above. In the calculation of oil yields from cottonseed it is necessary to assume an arbitrary loss of oil in the oilcake. It is customary to express the efficiency of oil extraction in terms of "press-room standards" (per cent oil divided by per cent ammonia content of the seed) as indicated in Table 102. The available oil per ton of cottonseed is found by subtracting from total oil in the seed the pounds of oil in the cake and hulls corresponding to the ammonia content of the seed, as shown in Table 102. As an example:

Analysis of the seed:

Ammonia 3.50%
Oil 18.6%

Calculation of cake yield:

Available ammonia = (3.50%)(0.94) = 3.29%
Yield of ammonia per ton of seed = (0.0329)(2000) = 65.8 lbs.
Yield of 8% ammonia cake per ton of seed = 65.8/0.08 = 822 lbs.

Calculation of oil yield:

Total oil per ton of seed = 372 lbs.
Oil lost in cake and hulls (from Table 136) = 57 lbs.
Available oil = 372 minus 57 = 315 lbs.

TABLE 102[a]

The table shows the press-room standards (per cent oil divided by per cent ammonia in cake) for varying ammonia percentages in seed. It also shows the pounds of oil left in cake plus a constant of 4 pounds of oil left in hulls. This weight of oil in cake for any given per cent ammonia in seed is a constant for cake of any ammonia content.

Total ammonia, %	Available ammonia 94% of total, %	Press-room standard	Pounds oil in 8% cake and hulls
2.80	2.63	87	50
2.85	2.68	87	50
2.90	2.73	86	51
2.95	2.77	86	51
3.00	2.82	85	52
3.05	2.87	85	53
3.10	2.91	84	53
3.15	2.96	84	54
3.20	3.01	83	54
3.25	3.06	83	55
3.30	3.10	82	55
3.35	3.15	82	56
3.40	3.20	81	56
3.45	3.24	81	56
3.50	3.29	80	57
3.55	3.34	80	57
3.60	3.38	79	57
3.65	3.43	79	58
3.70	3.48	78	58
3.75	3.52	78	59
3.80	3.57	77	59
3.85	3.62	77	60
3.90	3.67	76	60
3.95	3.71	76	60
4.00	3.76	75	60
4.05	3.81	75	61
4.10	3.85	74	61
4.15	3.90	74	62
4.20	3.95	73	62
4.25	3.99	73	62
4.30	4.04	72	62
4.35	4.09	72	63
4.40	4.13	71	63
4.45	4.18	71	63
4.50	4.23	70	63
4.55	4.28	70	64
4.60	4.32	69	64
4.65	4.37	69	64
4.70	4.42	68	64
4.75	4.47	68	65
4.80	4.51	67	65

[a] National Cottonseed Products Assoc., *Rules Governing Transactions between Members* (1949–1950).

In the case of peanuts, the available ammonia is taken as 97% of the total ammonia as shown by analysis. Of the total oil by analysis in each ton of seed it is assumed that 89.7 pounds will be lost in the hulls and retained in the cake and of the remainder it is assumed that 97% will actually be recovered.

Materials balances in actual oil milling operations on copra and peanuts have been reported by Sethne[46] and Dollear et al.,[47] respectively.

4. EVALUATION OF CRUDE AND REFINED OILS

Most of the trade in crude and refined oils in the United States is conducted with the aid of uniform standards, specifications, and trading rules established by various trade organizations and associated scientific or technical societies. The trading rules generally set forth specifications for different grades of each fat or oil, and in many cases they include systems for the establishment of premiums or penalties based on the contract price for oil that is better or poorer in quality than the standard for a common basis grade.

The greater part of the crude soybean, cottonseed, and peanut oil bought and sold for edible purposes in the United States is traded under the comprehensive rules of the National Soybean Processors Association (N.S.P.A.)[44] and the National Cottonseed Products Association (N.C.P.A.),[45] which not only specify grades, but also set up a schedule of premiums and discounts based upon laboratory refining tests on the oil. Refined domestic oils, imported vegetable oils, and inedible tallows and greases are generally traded under the less elaborate rules of the New York Produce Exchange (N.Y.P.E.).[48] The N.S.P.A. has specifications for soybean oil intended for paint manufacture or other industrial use. Similar specifications have been established by the American Society for Testing Materials (A.S.T.M.)[49] for other drying oils, including linseed, perilla, oiticica, and tung (see Chapter VI.)

Although not directly concerned with oil trading, the American Oil Chemists' Society (A.O.C.S.)[43] has for many years been active in the development and formulation of analytical methods which largely form the basis for the trading rules referred to above. Specifications based on A.O.C.S. methods, which include laboratory refining and bleaching test methods for a variety of fats and oils, are often written into contracts outside any of the various sets of official trading rules.

The present discussion will be limited to a brief review of the more

[46] M. Sethne, *Kgl. Norske Videnskab. Selskabs. Skrifter, 1939,* No. 3 (1940).
[47] F. G. Dollear, C. L. Hoffpauir, and R. O. Feuge, *Oil & Soap, 23,* 45–48 (1946).
[48] New York Produce Exchange. *Rules Regulating Business Among Members.*
[49] American Society for Testing Materials, *A.S.T.M. Standards, 1949, Part 4.* Philadelphia, 1950.

commonly used standards and rules in terms of the different analytical determinations, and will cover only practices in the United States; in Europe and elsewhere grading systems and trading rules for both oils and oil seeds are known to be generally much less elaborate and less generally employed. For more detailed information the reader is referred to the latest editions of the trading rules mentioned above, and for critical discussions of the relatively involved rules that have been developed for cottonseed and soybean oils, respectively, the publications of Barrow[50] and Freyer.[51]

(a) Identity and Type

In addition to the identity of the oil in question, contracts often specify a particular type, inasmuch as the properties and processing characteristics of oils may vary according to the geographical origin, as well as the method of extraction from the original oil-bearing material.

Palm oils, for example, are designated as native or plantation, and are further identified as Malayan, Congo, Lagos, Niger, etc., according to origin; each type has a more or characteristic range of free fatty acid content. Coconut oils are similarly identified as Ceylon, Cochin, etc.

Soybean oils are classified as expeller, hydraulic, or extracted, according to the method of recovery, and each of the three types may be degummed or undegummed. Cottonseed oil may be hydraulic or cold pressed, and hydraulic oils may be further designated as slow breaking by the vendor and subject to a modification of the regular laboratory refining test if they yield lower refining losses with prolonged stirring with lye.

The oil supplied must in all cases be an authentic oil of the kind contracted for. Oils with chemical and physical characteristics entirely out of line with accepted values, with a definite appearance, flavor, or odor of a foreign oil, or yielding an unmistakable color test or other identifying test for a foreign oil are generally rejectable.

(b) Free Fatty Acids

Standards for the content of free fatty acids are not generally specified in the case of crude oils sold on the basis of a refining test, as this value is significant chiefly in its relation to refining loss. Where refining tests are not employed, the content of free acids must serve as a rough indication of the loss to be expected. Contracts may be made with a maximum acidity specified or with a specific acidity designated as a basis for settlement. In the latter case, under the general N.Y.P.E. rules, a discount of

[50] E. R. Barrow, Chapter XI, in *Cottonseed and Cottonseed Products*, A. E. Bailey, ed., Interscience, New York, 1948.
[51] E. Freyer, Chapter XI, in *Soybeans and Soybean Products*, K. S. Markley, ed., Interscience, New York, 1950.

0.5% of the contract price is allowed for each 1% free fatty acids above the basis figure, with fractions in proportion.

Standards for different grades of inedible tallows and greases under the N.Y.P.E. rules (page 528) are based in part on the free fatty acids content, with the maximum values in different cases varying from 1 to 40%.

According to the N.C.P.A. rules, crude cottonseed oil containing over 3.25% free fatty acids is automatically graded "off" in flavor and made subject to a discount of 1.5% of the contract price.

Free fatty acids specifications for refined oils under rules of the N.C.P.A., N.S.P.A., N.Y.P.E., etc., are not exacting; a maximum of 0.10–0.25% is allowed in different cases, whereas careful alkali refining will readily reduce the free acids of any oil to less than 0.05%.

(c) Refining Loss

For many years trading rules of the N.C.P.A. have called for a standard laboratory refining test with caustic soda for crude cottonseed oils, with a loss of 9% being assumed for the basis grade (basis prime crude) and premiums or penalties (based on refined oil weight) assessed at the rate of 0.75% of the contract price for each 1% loss above or below this figure. The N.C.P.A. rule for crude peanut oil is similar, except for a basis loss of 5%, as is also the N.S.P.A. rule for crude soybean oil, except that the basis loss is 7% and allowances are based on the weight of the crude oil. In addition to these three oils, the A.O.C.S. has official refining test methods for coconut and corn oils, and the same basic test is also applicable, with suitable modifications, to other fats and oils.

As edible oils were formerly refined almost exclusively with caustic soda by batch methods, as the laboratory tests generally check well with batch plant refining results, and as oils of a given acidity may vary widely in refining loss, the standard laboratory refining test has in the past been rightly regarded as an almost-ideal quantitative criterion of crude oil value. However, it is less clearly a proper index in the light of the latest modern practice, which employs continuous centrifugal refining, often with soda ash rather than caustic soda alone, to attain refining losses considerably lower than those obtained by batch methods. It is also difficult to apply to certain soybean oils and other oils that yield a soft soapstock.

The evaluation of crude oils on the basis of a centrifugal laboratory refining test[52] or of the so-called Wesson loss (page 621)[53] has been urged. but not given official approval.

[52] Refining Committee, American Oil Chemists' Society, Oil & Soap, 18, 208–214 (1941); 19, 160–163 (1942); 20, 179–189 (1943); 21, 123–126 (1944); 22, 156–159 (1945); 23, 252–254 (1946). See also J. F. Johnson and S. T. Bauer, J. Am. Oil Chem. Soc., 26, 435–438 (1949).

[53] R. R. King, and F. W. Wharton, J. Am. Oil Chem. Soc., 25, 66–68 (1948).

(d) Color

The color of an oil is a legitimate factor in determining its value, inasmuch as dark oils require expensive processing for conversion to acceptable light-colored products, and dark color may be an indication of poor quality in other respects.

The carotenoid pigments and other pigments associated naturally with oils of good quality are removed with relative ease by conventional refining and more particularly by bleaching treatment, whereas the dark-colored degradation products that contribute much of the color to low-grade oils and fats are much more resistant to removal. For this reason, the color of an oil after refining and bleaching is a more satisfactory index of quality than is the color of the crude oil or the color after refining alone. Furthermore, there are few manufactured products in which light-colored oils are not at a premium; hence purely from the standpoint of appearance the response of an oil to bleaching is more important than its original color or its color prior to bleaching.

Colors determined according to the so-called FAC method (page 653) on the crude fat form part of the customary basis for grading inedible tallows and greases (page 149). N.Y.P.E. rules specify maximum colors for certain grades of crude coconut oil. Color grading of other crude oils is uncommon.

The N.C.P.A. rules establish a maximum Lovibond red color (page 652) of 7.6 for "basis prime crude cottonseed oil" and 5.0 for "basis prime crude peanut oil" refined by the official laboratory method, and assess penalties of 0.5% of the contract price for each unit of red color above these standards, but provide no premiums for better colors.

Under the N.S.P.A. rules for soybean oil all penalties for off-color are based upon the color of the oil after both refining and bleaching (RB color). To distinguish between normal yellow-red oils and oils with a predominantly greenish cast, a green color standard is provided, and crude oils darker than the standard are designated as green oils. Green oils lighter than a second darker standard are subjected to a discount amounting to 1% of the contract price; those darker than the second standard are subjected to a discount of 2%. Two laboratory bleaching methods are employed; normal oils or oils of the No. 1 prime color grade are bleached after refining with 6% of a standard fuller's earth; green oils of the No. 2 green color grade or the darker No. 3 color grade mentioned above are similarly bleached with 4% of a standard activated earth with greater adsorptive power, especially for green pigments. Penalties for off-color begin above a Lovibond red color of 3.5 for normal oils and above a color of 2.0 for green oils, and range from 0.05 to 0.15% of the contract price for each 0.1 unit of color above the standards.

The use of RB colors as a more rational basis for trading has been

advocated for both cottonseed oil[54] and inedible tallows and greases.[55] In the case of cottonseed oil there is normally a fairly good correlation between RB colors and the refined oil colors used at present in trading, but frequently "color reverting" oils (page 522) are encountered which are more difficult to bleach than the refined oil color would indicate. In the case of inedible animal fats the establishment of grades purely upon the basis of crude oil colors is objectionable because of a generally poor correlation with the RB colors in which processors of high-grade soaps are primarily interested, and also because such a grading system does not prevent the unethical renderer from partially bleaching his fats to a higher grade and thus supplying the purchaser with a material with a poorer response to further treatment than a normal fat of the same color.

In refined oil trading, the Lovibond red color limits set for "prime summer yellow cottonseed oil" and "prime yellow peanut oil" under N.C.P.A. and N.Y.P.E. rules are the same as those for the prime crude oils after laboratory refining, *viz.*, 7.6 and 5.0, respectively. Under the N.Y.P.E. rules the color limit for "prime refined corn oil" is 7.6 red. Tentative N.S.P.A. specifications for "refined soybean oil" require minimum bleach colors of 3.5 red with standard fuller's earth for normal oils and 2.0 red with standard activated earth for green oils. The N.Y.P.E. rules require all "bleachable refined soybean oil" to bleach to a color of 2.0 red with standard activated earth. Under N.C.P.A. and N.Y.P.E. rules "bleachable prime summer yellow (refined) cottonseed oil" must bleach to a color of 2.5 or better with standard fuller's earth, and "prime summer or winter white (refined and bleached) cottonseed oil" must have a similar color.

(e) *Moisture and Insoluble and Unsaponifiable Material*

In crude oils sold on the basis of refining loss no account is taken of moisture and insoluble impurities in the oil; in other oils due allowance is made in some cases if such material exceeds a minimum amount, *e.g.*, 2% in the case of palm oil shipped in barrels or casks, under N.Y.P.E. rules.

Refined oils are generally expected to be virtually anhydrous, *e.g.*, N.C.P.A., N.S.P.A., and N.Y.P.E. rules allow a maximum of 0.10% moisture in refined cottonseed, soybean, and peanut oils, which is less than the amount which will dissolve at ordinary atmospheric temperatures.

In the case of inedible tallows and greases, which are used principally for soapmaking, the moisture, insoluble impurities, and unsaponifiable material are taken together in the so-called MIU value, for which maximums are set for different grades (Chapter VI).

[54] R. R. King, *J. Am. Oil Chem. Soc.*, 25, 4–6 (1948).
[55] L. B. Parsons, *Oil & Soap*, 20, 256–257 (1943).

(f) Titer

The titer is an important characteristic of inedible fats used for soap-making or as raw materials for fatty acid manufacture, and is also an indication of the firmness of natural edible fats such as lard. Under the accepted United States trading rules, inedible fats with titers below 40°C. are classed as greases, and those with higher titers are classed as tallows. Minimum titers are also specified for the different grades (Chapter VI).

(g) Iodine Value. Unsaturation

The iodine value is an index of the drying and polymerizing properties of oils such as linseed and soybeans; hence the A.S.T.M. specifications for such oils specify an iodine value range, and contracts often mention a minimum iodine value. Because of their peculiar chemical constitution, the iodine value does not similarly evaluate conjugated acid oils such as tung or oiticica, or reveal adulteration with a cheaper oil. Specifications for these oils are usually based upon a heating or solidification test (page 177) indicative of the polymerizing properties. (See Chapter VI.)

(h) Miscellaneous Characteristics

Substantial removal of solvent from a solvent-extracted oil is best assured by the specification of a minimum flash point. The present N.S.P.A. rules for solvent-extracted soybean oil require that the flash point by an open-cup method shall not be below 250°F.

The standard cold test (hours at 32°F. without clouding) for "winter" cottonseed oil, i.e., oil subjected to fractional crystallization for the removal of high-melting glycerides, is 5.5 hours under N.C.P.A. and N.Y.P.E. rules. Good commercial oils commonly have a much higher cold test.

A low content of "break material" (heat-coagulable phosphatides, etc.) is desirable for paint or varnish oils if they are to be used without refining. A maximum amount of break material is often specified for drying oils, e.g., 0.6% for soybean oil intended for industrial use under the N.S.P.A. specifications.

The A.S.T.M. specification for raw linseed oil includes maximum values for "foots" or acetone-insoluble material as determined by a special procedure at two different temperatures. The A.S.T.M. method for the determination of foots has never been entirely satisfactory; a modification involving centrifugal separation rather than separation by gravity settling has been proposed by Freyer and Shelburne.[55a]

[55a] E. Freyer and V. B. Shelburne, J. Am. Oil Chem. Soc., 27, 545–550 (1950).

C. Handling and Storage

1. Shipping, Receiving, and Sampling

In the United States soybeans and flaxseed are handled very much like wheat or other cereal grains, and are usually received at the oil mills in railroad cars. This mode of handling tends to concentrate receipts at relatively few centers and to make many of the mills large. Cottonseed and peanuts, on the other hand, are so bulky as to discourage long-range shipment. The mills are distributed throughout the territory of production, and are frequently small, with the bulk of shipments being by motor truck.

In the United States and elsewhere imported oil seeds are almost always transferred directly from ships to storage facilities at the oil mills; this tends to place oil production in the hands of large establishments located in seaports. Preceding ocean shipment, the oil seeds are usually collected from scattered sources at a number of central points. The long time elapsing between harvesting and shipment and the difficulty of properly supervising collection, drying, and handling in the initial stages account for the fact that imported seeds are generally inferior in quality to domestic seeds.

At large mills railway cars are generally unloaded by gravity with the aid of mechanical car dumpers. Mechanical dumpers are also often used with trucks. Where dumping is not feasible, use is made of various types of conveyors, power shovels, etc. The conveyors used for unloading and for transferring material within the mill are of both the mechanical and pneumatic types; the latter require more power for operation, but have the advantage of dependability and great flexibility. In addition they tend to cool and partially dry the seed, which is often an advantage. For detailed information on the handling of two representative seeds, cottonseed and soybeans, the reader is referred to the publications of Alderks[28] and Holman.[30]

Oil seeds must be sampled upon receipt, both to determine their value and to permit segregation of different shipments according to their quality and probable tendency to deteriorate in storage; the latter is particularly important in the case of cottonseed. The proper sampling of oil seeds is by no means easy, and official trading rules of such organizations as the N.C.P.A. and the N.S.P.A. specify in detail not only methods for analysis and grading, but also standard sampling methods, and provide for official weighers and samplers.[56] Copra is a particularly difficult material to sample adequately, because of its peculiar size distribution, its susceptibility to uneven mold deterioration, and the tendency of fine

[56] See R. T. Doughtie, Jr., *J. Am. Oil Chem. Soc.*, *24*, 335–340 (1947).

material to deteriorate more rapidly than large pieces. Techniques for copra sampling have been discussed by Tompkins.[57]

Either bomb or core samplers may be used for drawing samples of oil before unloading. However, the usual core sampling method for tank car shipments is subject to a geometric error, *i.e.*, a core taken from a horizontal cylindrical tank represents a disproportionately large amount of the extreme bottom layer of the tank, and this may lead to serious errors if the bottom layer contains much settlings.[58,59] A bomb sampling method that compensates for this error has been proposed by Freyer.[59] The presence of an undue amount of settlings in a sample of oil sold upon the basis of refining loss serves to decrease the apparent value of the oil out of proportion to the actual amount of settlings, because of the tendency of the latter to induce hydrolysis in the oil and the large effect of a small amount of settlings on the refining loss.[58,60]

The sampling of oil in barges or seagoing tankers must be carried out with bomb samplers, and is a more difficult matter than the sampling of tank cars. Techniques for tanker sampling have been described by Tompkins.[61]

Virtually all the crude oil sold in the United States, and most refined products sold in bulk are shipped in standard 8,000-gallon tank cars holding 60,000–61,000 pounds of oil.

The transoceanic shipment of oils is, of course, most economically carried out in tankers. However, much oil is handled in barrels, drums, hogsheads, etc., particularly if it is high melting enough to become solid or semisolid upon cooling. The most common package consists of iron-bound hardwood barrels of 45–58 gallons capacity. Liquid oils received in drums are usually unloaded by gravity into troughs placed under special unloading racks, from which the oil flows to tanks. If there is possibility of a solid residue remaining, the drums are steamed before they are removed from the rack. Solid fats in barrels are unloaded by stripping the staves from the fat to leave a solid cake, which is then dumped into a heated tank. Liquid oils in tankers are, of course, pumped out. Tank cars are usually pumped also, after melting the fat with the internal steam coils always provided in the tank, if the fat happens to be partially solidified. However, tank cars at some refineries are dumped by gravity into unloading troughs underneath the tracks, from which the oil is pumped to a storage or holding tank.

[57] P. W. Tompkins, *Oil & Fat Inds.*, *4*, 23–28 (1923); *Oil & Soap*, *18*, 103–106 (1941).
[58] E. R. Barrow, *Oil & Fat Inds.*, *4*, 383–385 1923.
[59] E. Freyer, *J. Am. Oil Chem. Soc.*, *26*, 408–413 (1949).
[60] E. R. Barrow, *Cotton Oil Press*, *11*, No. 7, 21–23 (1927).
[61] P. W. Tompkins, *Oil & Soap*, *23*, 35–37 (1946).

2. Storage of Oil Seeds

(a) Cleaning and Drying

It is always desirable to clean oil seeds and remove plant stems and foliage and other trash before the seeds are stored, as such material tends to decompose and initiate heating in the seed mass. Elevators handling such oil seed as soybeans and flaxseed commonly are supplied with seed cleaning equipment, but precleaning of seed before they are stored is the exception rather than the rule in the case of cottonseed, because of the greater difficulty in cleaning and the heavy influx of seed to the mills over a short period of time.

For the same reason, cottonseed mills are less commonly equipped with seed dryers than mills and elevators handling soybeans or other seed which are similar to the cereal grains. Seed dryers may be either steam-heated or gas- or oil-fired, with direct heating. They consist essentially of some mechanical means for dispersing the continuously flowing mass of seeds and a blower for forcing hot air or flue gas through and over the seeds. Drying is usually conducted at about 220–230°F., after which the seeds are cooled to within 10–15°F. of the atmospheric temperature by the forced circulation of air. Seeds that have heated prior to their receipt at the mill may be cooled and reduced 1–2% in moisture content by simply passing them through a dryer with the blowers operating but the heating unit out of service. For details of dryer construction and operation, reference may be made to Alderks[28] and Holman.[30]

It may be mentioned that the object in drying oil seeds for storage is by no means the substantial removal of moisture, but merely reduction of the moisture content below a more or less critical level for safe storage. This may involve the removal of only a minor fraction of the total seed moisture.

The drying of copra prior to shipment presents a particular problem, inasmuch as the coconuts are harvested with the oily portion of the seed at a high moisture content. Part of the copra reaching the market is sun-dried, and part is artificially dried. Generally, the drying or curing process is carried out by rather primitive means, and the quality of the product is subject to wide variation according to the vagaries of the weather and the care exercised in carrying out the process. Palm kernels are ordinarily air-dried by storage in small bins with free circulation of air before they are bagged by shipment. The general use of modern forced drying equipment would undoubtedly do much to improve the quality of both copra and palm kernels.[62]

[62] For a discussion of practices and problems in the drying of tropical oilseeds, see A. C. Barnes, *Trans. Inst. Chem. Engrs.* (London). *6*, 177–184 (1928).

(b) Storage Structures

Seeds such as flax, sunflower, and soybeans are stored satisfactorily in more or less standard grain elevators. However, cottonseed requires special seed houses provided with a system of air ducts and large cooling fans for displacing the interstitial air with cold air from the outside as early in the season as such air is available, and for cooling portions of the seed that show a disposition to undergo heating thereafter. The design and operation of seed houses and air cooling equipment are discussed in detail by Alderks.[28]

Seeds such as palm kernels, tung nuts, etc., which are harvested at a high moisture content, must first be stored for a considerable period in small bins with free access to air, to permit air drying to take place, unless they are dried by artificial means.

(c) Inhibition of Action of Enzymes and Microorganisms

Since both enzymes and microorganisms are readily inactivated by exposure to high temperatures, it would appear that a simple heat treatment of oil seeds prior to storage might prove highly beneficial to their storage properties. In practice, however, the problem is by no means so simple. The heat treatment itself creates conditions favorable to deteriorative processes; hence, as pointed out by Altschul,[5] unless it is both rapid and completely effective, it may well leave the seeds in such condition that subsequent deterioration will be accelerated rather than inhibited. Both enzymes and microorganisms are distributed more or less throughout the seed; hence mere surface sterilization does not suffice. Heat penetration with ordinary methods of heating is relatively slow and, actually, experiments in heating and heat drying to improve the storage characteristics of oil seeds have not consistently yielded benefits greater than could be attributed to drying alone. In some cases heat treatment alone has proved harmful.[63]

In an effort to overcome the difficulty created by the poor thermal conductivity of cottonseed, Lyman and co-workers[64] conducted a series of experiments in which very rapid treatment was achieved by dielectric heating. Internal seed temperatures above 100°C. were readily obtained within one minute, and the treatment was highly effective in preventing lipolysis upon subsequent storage of the seed. However, high equipment and power costs make the method uneconomic at present.

[63] See F. R. Robertson and J. G. Campbell. *Oil & Soap, 10,* 146–147 (1933).
[64] C. M. Lyman, E. J. Burda, and P. Q. Olschner, *J. Am. Oil Chem. Soc., 25,* 246–249 (1948).

Roberts and co-workers[65] have reported that the very active lipase in rice bran is inactivated by exposure of either the separated bran or the rough rice to steam at 212°F. for one minute.

A highly interesting approach to the problem of oil seed deterioration involves the chemical inhibition of biological activity.[66] This method is still in the developmental stage, but appears to offer considerable promise, particularly as applied to cottonseed of high moisture content. Among the more effective inhibitors thus far discovered are propylene glycol dipropionate and 4,6-*bis*-chloromethylbenzene or -xylene. These compounds, incorporated to the amount of about 0.3% of the weight of the seed, have been found to suppress heating and lipolysis to a remarkable degree. A synergistic effect has been observed with the two compounds mentioned. Neither appears to be toxic.

The use of mold inhibitors in the storage of cereal grains has been studied by Milner and co-workers.[67]

3. Storage of Other Oil-Bearing Materials

Oil-bearing materials other than oil seeds are seldom stored except for very short periods. The low-temperature storage of fatty tissues, etc., will decrease the rate of deterioration through lipolysis, but if the fat-bearing material must be accumulated over a period of hours before a batch can be rendered, it is usually better practice to charge it to the rendering vessel as it becomes available, and quickly heat it to a temperature sufficiently high to inactivate enzymes.

The data of Vibrans[37a] on the rates of lipolysis in different fatty tissues (of the hog) stored at 34°F. are shown in Figure 62 (page 520). Other data of Vibrans show that in leaf fat free fatty acids increase approximately 5 times as fast at 72–74°F. as at 34°F.

Fish livers of high vitamin A content present an exception with respect to the length of the storage period. These are often collected at widely scattered points and forwarded to central processing plants in a frozen condition.

4. Storage of Oils

The storage of crude and refined fats and oils has been discussed previously. Ordinarily vegetable oils of high tocopherol content, if

[65] R. L. Roberts, G. R. Van Atta, I. R. Hunter, D. F. Houston, E. B. Kester, and H. S. Olcott, *Food Inds.*, *21*, 1041 (1949).

[66] A. M. Altschul, *Cotton Gin and Oil Mill Press*, Jan. 8, 1949. M. Z. Condon, F. R. Andrews, M. G. Lambou, and A. M. Altschul, *Science*, *105*, 525–527 (1947). M. Kulka, *Can. J. Research*, *B23*, 106–110 (1945).

[67] M. Milner, C. M. Christensen, and W. F. Geddes, *Cereal Chem.*, *24*, 507–517 (1947).

clean and dry, can be stored in large tanks for extended periods without serious deterioration. Animal fats, which are deficient in antioxidants and which oxidize more readily, store less satisfactorily. The large American meat packers generally provide refrigerated storage tanks for lard. The storage of lard or other high melting fats is made more difficult by the necessity of heating the tank each time that a portion of fat is withdrawn.

EXTRACTION OF FATS AND OILS[1]

The separation of oils and fats from oil-bearing animal and vegetable materials constitutes a distinct and specialized branch of fat technology. The widely differing characteristics of different fatty materials have given rise to such diverse extraction processes as rendering, pressing, and solvent extraction. However, all extraction processes have certain objects in common. These are, first, to obtain the oil uninjured and as free as possible from undesirable impurities; second, to obtain the oil in as high a yield as is consistent with the economy of the process; and third, to produce an oil cake or residue of the greatest possible value.

Fatty animal tissues consist largely of fat and water, which may be separated from the solid portions of the tissue and from each other with relative ease, by one of the rendering processes. The extraction of vegetable oils is a more difficult matter. Vegetable materials, and in particular some of the oil seeds, contain a large proportion of solid material associated with the oil. Careful reduction of the material, followed by heat treatment and the application of heavy pressure, is required to obtain an efficient separation of the oil from the solids.

Even after the most efficient pressing, an oil cake will retain an appreciable amount of absorbed oil; the latter will usually amount to 4–7% of the weight of the cake. In the case of seed or other materials initially high in oil and low in solids content, the unextracted residue will be but a small fraction of the total oil. However, in seeds of low oil content, for example, soybeans, it may constitute as much as 20–25% of the oil. For the processing of low-oil seeds, solvent extraction is particularly valuable, since it will reduce residual oil in the extracted seeds to less than 1%. The

[1] GENERAL REFERENCES: O. H. Alderks, Chapter XV, in *Cottonseed and Cottonseed Products*, A. E. Bailey, ed., Interscience, New York, 1948. H. N. Brocklesby, *The Chemistry and Technology of Marine Animal Oils*, Fisheries Res. Board of Canada, Ottawa, 1941. R. Heublyum and R. Japhe, *Allgem. Oel- u. Fett-Ztg.*, *32*, 401–405, 447–452, 497–502 (1935); *33*, 13–17, 49–55, 96–103, 141–149, 199–203, 254–261 (1936). L. F. Langhurst, Chapters XIV and XV, in *Soybeans and Soybean Products*, K. S. Markley, ed., Interscience, New York, 1950. H. Schönfeld, ed., *Chemie und Technologie der Fette und Fettprodukte*, Vol. I, *Chemie und Gewinnung der Fette*, Springer, Vienna, 1936. M. K. Thornton, Jr., *Cottonseed Products*, Oil Mill Gazetteer, Wharton, Texas, 1932. A. C. Wamble, Chapter XIV, in *Cottonseed and Cottonseed Products*, A. E. Bailey, ed., Interscience, New York, 1948. W. R. Woolrich and E. L. Carpenter, *Mechanical Processing of Cottonseed*, Engineering Expt. Sta., Univ. of Tennessee, Knoxville, 1935.

chief disadvantages of solvent extraction are the high initial cost of the equipment, and the circumstance that some oil seeds are inclined to disintegrate under the influence of the solvent, and consequently are difficult to handle.

There are a number of more or less critical operations in oil milling which are auxiliary to the actual expression or extraction. Wherever possible it is desirable to decorticate oil seed before the oil is removed in order both to increase the capacity of the extraction equipment and to avoid loss of oil through absorption by the hulls. The seeds must then be rolled, ground, or otherwise reduced to fine particles. After they are reduced, they must be given heat treatment, to make the walls of the oil cells permeable to the oil and to render the oil free-flowing, unless they are to be solvent extracted, in which case heat treatment is not generally necessary. In the case of cottonseed, special attention must be given to the inactivation of gossypol or other toxic constituents.

In the extraction of oil from oil seeds there are considerable differences between common American and common European practice. These are the result of basic differences in the supply of oil seeds. Most American mills operate on domestic oil seeds. The mills are usually located close to producing areas; frequently but one type of oil seed is processed, the quality of the seed is generally high, and there is relatively little variation in the characteristics of the seed through the processing season, or from one season to another. European mills, on the other hand, process imported oil seeds almost exclusively, and each mill must be prepared to handle a variety of oil seeds, each of which may vary widely in quality and processing characteristics. As a result, American milling practice has become highly specialized, with the object in each case being to place a more or less specific operation on a plane of highest possible efficiency. In European mills it has been necessary to make some sacrifice of operating efficiency in favor of flexibility of operation. This accounts for the greater use in Europe of cage-type as opposed to open-type batch presses; for the employment in Europe of multi-stage continuous pressing, as compared to single-stage high-pressure pressing in America; and for recent efforts of American processors to apply solvent extraction directly to high-oil seeds which in Europe are commonly prepressed before they are extracted.

The average yields of oil obtainable by commercial extraction methods from a number of common oil seeds are summarized in Table 103. Certain comparative data on whole seeds and kernels may be found in Table 104, page 545. For information on yields from fruit pulps and animal sources, reference may be made to the specific fats and oils, in other portions of this chapter and in other chapters.

It is probable that the first methods of oil extraction were rendering

procedures practiced by primitive man, following cooking techniques developed for the preparation of meats for food. The pressing of olive pulp for oil probably antedated the pressing of oilseeds, although seeds were processed in mechanical presses operated by wedges or levers by the Chinese and others at an early date. On the other hand, the more efficient hydraulic operation of mechanical presses was not adopted until early in the 19th century. The continuous screw press is a modern development, while the solvent extraction of oil seeds on a large scale was not a reality until after World War I. A brief review of the history of oil seed processing was published recently by Goss.[1a]

The residues from the processing of oilseeds or animal tissues for fat are generally high in protein content and are in good demand as animal feedstuffs. They have a limited use as a source of human food (soybean or cottonseed flour), or as a source of industrial proteins (*e.g.*, for making glues). The residues from castor beans and tung nuts are toxic unless specially treated, and hence are used only as a fertilizer, etc.

TABLE 103

AVERAGE YIELD OF OIL FROM COMMERCIAL PROCESSING OF COMMON OIL SEEDS
(PER CENT OIL FROM SEED OF NORMAL MOISTURE CONTENT)[a]

Babassu (kernels)	63	Peanuts	35
Castor beans	45	Perilla seed	37
Coconut (copra)	63	Poppyseed	40
Corn (germs)	45	Rapeseed	35
Cottonseed	16	Rice bran	14
Flaxseed	34	Safflower seed	28
Hempseed	24	Sesame seed	47
Kapok seed	20	Soybeans	18
Oiticica (kernels)	60	Sunflowerseed	25
Palm, African (kernels)	45	Teaseed	48
		Tung	35

[a] Yields are by mechanical expression for all except soybeans and rice bran, which are by solvent extraction, and refer to whole or undecorticated seeds, unless otherwise stated.

A. Mechanical Pretreatment

1. PREPARATION OF ANIMAL MATERIALS

Fatty animal materials, as compared with oil seeds and other vegetable materials, require comparatively little preparation prior to the rendering operation. Fatty stock destined for the production of neutral, low-temperature-rendered fats, such as oleo stock or lard, is trimmed quite care-

[1a] W. H. Goss, *Proceedings of a Six Day Short Course in Vegetable Oils*, American Oil Chemists' Society, University of Illinois, 1948, pp. 52–56.

fully, and washed before it is charged to the rendering units. Ordinary stock, such as that used in making prime steam lard, is not always washed and is less carefully trimmed.

In the larger establishments the stock to be rendered is sorted into different classes of material, partly in order to avoid mixing high quality materials with those of low quality, and partly because some stocks, such as those containing large bones, require more severe rendering treatment than others.

In either dry rendering or steam rendering, separation of the fat is more rapid if the fatty stock is first cut into small pieces, although ordinarily in steam rendering this operation is omitted. Prolonged wet rendering under pressure will disintegrate even large bones or whole carcasses, so that the preparation of stock for this process is not extremely critical.

Rotary hashers, similar in principle to ordinary household food choppers are used for the reduction of stock which is free from bones. The degree of reduction is much coarser than that employed in the processing of oil seeds; the dimensions of the hashed pieces may be measured in large fractions of inches or even in inches. Most animal materials disintegrate quite readily. Whale blubber is particularly tough and requires more drastic treatment. Blubber presses, consisting of heavy corrugated rolls, are now in use.[2] Passage of large chunks of blubber through these rolls reduces them to semifluid condition, and decreases the rendering time.

2. Preparation of Oil Seeds

(a) Cleaning

The first step in the processing of oil seeds is cleaning of the seeds to separate foreign material. Sticks, stems, leaves, and similar trash are usually removed by means of revolving screens or reels. Sand or dirt is also removed by screening. Electromagnets installed over a conveyor belt are used for the removal of tramp iron. Special "stoners" are employed for taking out heavy stones and mud balls from shelled peanuts. As stated previously, the cleaning of oil seeds is preferably carried out before the seeds are placed in storage.

(b) Dehulling and Separation of Hulls

Oil seeds are preferably decorticated before they are extracted, wherever this is practicable. The hulls of oil-bearing seeds are low in oil content, usually containing not more than about 1% oil. An oil content of 22%

[2] H. N. Brocklesby, *The Chemistry and Technology of Marine Animal Oils*. Fisheries Research Board of Canada, Ottawa, 1941.

has been reported[2] in the hull of the flaxseed. However, this is not be-
lieved to represent a true value for the hull; it appears rather to be due to
a part of the oily endosperm of the kernel remaining attached to the sepa-
rated hull. If the hulls are not removed from the seeds before the latter
are extracted they merely reduce the total yield of oil by absorbing and
retaining oil in the press cake, and in addition they reduce the capacity
of the extraction equipment.

The hulling machines used for the decortication of medium-sized oil
seeds with a flexible seed coat, such as cottonseed, peanuts, and sunflower
seed, are of two principal types: bar hullers and disc hullers.

The rotating member of a bar huller consists of a cylinder which is
equipped on its outer surface with a number of slightly projecting, longi-
tudinally placed, sharply ground, square-edged knives or "bars." Opposed
to the cylinder over an area corresponding to about one-third of its surface
is a concave member provided with similar projecting bars. The seeds are
fed between the rotating cylinder and the concave member, and the hulls
are split as the seeds are caught between the opposed cutting edges. The
clearance between the cutting edges is of course variable for seeds of
different size.

The disc huller is more or less similar in principle to the bar huller,
except that the cutting edges consist of grooves cut radially in the surfaces
of two opposed and vertically mounted discs, one of which is stationary
and the other rotating. The seeds are fed to the center of the discs and
are discharged at their periphery by centrifugal force. With either type
of huller the condition of the seed is somewhat critical. Wet seed are
difficult to split cleanly, and are inclined to clog the huller, particularly
if it is of the disc type. On the other hand, if the seed are very dry, the
kernels are inclined to disintegrate to an excessive extent.

Different seeds vary considerably in the readiness with which they fall
out of the split hulls. Peanuts, for example, are quite loose in the shell
and separate readily. Cottonseed kernels or "meats" are more adherent
to the hull; consequently the hulls are customarily passed through a hull
beater to detach small meat particles after the first separation of hulls
and meats by screening. The separation systems used for cottonseed,
peanuts, etc., consist of various combinations of vibrating screens and
pneumatic lifts. It is necessary not only to separate the hulls from the
meats, but also to separate and recycle a certain proportion of uncut seeds
which escape the action of the huller. In the case of cottonseed the follow-
ing separations are commonly carried out: (a) separation of large meat
particles from hulls and uncut seed by screening; (b) separation of hulls
from uncut seed by an air lift; (c) separation of small meat particles from
hulls by beating and screening; and (d) separation of hull particles from
meats by air.

In practical mill operation, the greatest yield of oil is obtained by nicely balancing the degree of separation attained. If an attempt is made to separate hulls from the meats too cleanly, there will be a loss of oil due to meats being carried over into the hulls. If an excessive proportion of hulls is left in the kernels there will likewise be an undue loss of oil from absorption by the hulls. Under certain conditions, there may be an appreciable loss of oil due to absorption by the hulls as the latter come into contact with the oily meat particles during the separation operation. It is generally advisable to effect the separation of kernels and hulls as quickly as possible after the seeds are hulled, in order to avoid excessive contact between hulls and kernels or kernel particles.[2a]

TABLE 104

APPROXIMATE PROPORTIONS OF HULL AND KERNELS IN DIFFERENT OIL SEEDS, AND OIL CONTENTS OF WHOLE SEED, KERNELS, AND HULLS

Oil seeds	Per cent kernel	Per cent hull	Per cent oil in		
			Whole seed	Kernel	Hull
Usually decorticated:					
Oil palm	25	75	—	48	—
Babassu	9	91	—	67	—
Cohune	10	90	—	67	—
Tucum	30	70	—	47	—
Murmuru	40	60	—	—	—
Tung	60	40	30	50	—
Oiticica	65	35	38	58	—
Cacao beans	88	12	50	—	—
Castor beans	70–80	20–30	40–50	—	—
Cottonseed (delinted)	62	38	19	30	1–2
Peanuts	75	25	38	50	0.5–1
Sunflowerseed	45–60	40–55	22–36	36–55	1–2
Kapok	60	40	20–25	40	—
Safflower	50	50	28–33	55–65	1.5–2
Usually not decorticated:					
Soybeans	93	7	18	—	0.6
Flaxseed	57	43	—	58	22
Perilla seed	68	32	34	—	—
Hemp seed	62	38	31	—	—
Rapeseed	82	18	42	—	—
Mustard seed	80	20	—	—	—

Cottonseed are invariably delivered to the mills from the gins without removal of their coating of short fibers or linters, and must be delinted before they are hulled. Delintering machines (known as "linters") are

[2a] T. Arentz and J. Lund, in H. Schönfeld, ed., *Chemie und Technologie der Fette und Fettprodukte*, Vol. I, Springer, Vienna, 1936.

similar in principle and appearance to cotton gins, consisting essentially of a revolving assembly of closely spaced circular saws which pick the lint from the seed. A cylindrical brush revolving slightly faster than the saw assembly is provided to remove the lint from the saw teeth. The lint is blown from the brush to the surface of a perforated "condenser" drum, and continuously removed from the surface of the drum in the form of a roll. The lint is not ordinarily removed from the seed in a single operation, but is taken off in two or three cuts. Each successive cut is of lower grade than the cut preceding it, since increasing quantities of hull material are removed by the saws as delinting proceeds.

Soybeans are not ordinarily decorticated before they are processed for oil, except in cases in which the meal is destined for human consumption, because the hull constitutes but a small part of the seed and is relatively nonabsorbent. Small oil seeds, such as flaxseed, perilla seed, rapeseed, sesame seed, etc., are also processed without decortication. In some cases it would doubtless be desirable to hull the small seeds, if this could be done economically, but so far the process has been considered impracticable. Owen[3] has reported a series of experiments in the dry decortication of flaxseed and other small oil seeds, in an experimental machine of unspecified design. He concluded that hulling of linseed is impracticable because a large portion of the total oil is contained in the separated hull, but suggested that it might prove advantageous in the case of certain other small seeds, for example, hempseed.

The various palm kernels, such as oil palm or African palm kernels, babassu kernels, cohune kernels, etc., constitute a special class of oil seeds, since they are of relatively large size and are surrounded by a particularly hard, thick shell. Owing to the cheapness of labor in the producing regions, the large size of the nuts, and the refractory nature of the shells, these nuts are often cracked and the kernels separated by hand. Thus the entire production of Brazilian babassu kernels, amounting in some seasons to as much as 25,000 tons, has in the past been separated in this manner.

Nuts of the oil palm, which are less thick shelled than most of the American palm nuts, are apparently cracked to some extent by hand in Africa, but on the plantations of the East Indies and British Malaya they are usually cracked by machine. In one type of machine the nuts are fed to the center of a rotor provided with curved baffles, along which the nuts are flung out against a heavy steel housing and broken by impact. Another type of machine is simply a special type of hammer mill. The rotor consists of a frame supporting four heavy steel paddles. The nuts are dropped into the path of the paddles and cracked by impact. After

[3] G. W. Owen, *Oil & Soap, 16,* 55–58 (1939).

the nuts are cracked they are dropped to rotary screens, where some separation of kernels and shells is obtained. A considerable proportion of shell fragments, however, cannot be separated by screening. Owing to the high density of the shells, air separation, such as is used on cottonseed and peanuts, etc., is likewise ineffective in producing a further separation. There are two methods in vogue for separating palm kernels from shell fragments of a size comparable to that of the kernels. The dry method takes advantage of the fact that the kernels are rounded and inclined to roll easily, whereas the pieces of shell are flat and sharp edged, and hence do not as readily roll on an inclined surface. Dry separators consist of inclined belts provided with sharp projections, which move continuously upward. When a mixture of kernels and seeds is fed onto the surface of the belt, the kernels are inclined to roll down the belt, where they are collected at the lower end, whereas the fragments of shell are caught on the projections and carried over the top of the belt into a separate bin. Means must be provided for recycling of material after both the cracking and separating operations, since neither cracking nor separation is complete after one passage of the material through the machines.

The alternative method of separation consists of floating the kernels from the more dense shells in brine solution. The flotation method has the advantage of producing a clean separation of kernels and shells, but the kernels separated by this process must be dried before they can be stored or shipped.

The American palm nuts of the *Attalea* family, including the babassu and cohune, are excessively thick shelled and most difficult to decorticate by machinery. The babassu is particularly difficult because it contains several kernels, each of which is enclosed in a separate cavity within the shell. Whereas the splitting of an oil palm nut or most cohune nuts along a single plane of cleavage will usually free the kernel, the similar splitting of a babassu nut may not release a single one of its four to eight kernels. Recently a number of different machines have been devised for cracking American palm nuts. The machines designed for round nuts of the coyol type have either been of the centrifugal or hammer mill design, or have utilized the positive action of mechanically or hydraulically operated hammers striking against the nut as it is confined against a stationary anvil member. Some of the machines designed for cohune or babassu nuts employ chisel-like cutting edges to open the shell. One type of babassu opening machine has opposed cutting edges which split the nut into a number of segments, like those of an orange. Other machines for cohune and babassu nuts employ the hammer mill principle. These machines break up the kernel rather badly, and thorough drying of the kernels is depended upon to inhibit excessive enzyme action in the broken kernels during shipment.

In the case of any variety of palm nut, adequate drying of the nuts prior to cracking is highly essential, to insure that the kernel will not adhere to the shell. The kernels shrink considerably in drying and thus break away from the shell. Green or undried kernels fill the shell cavity tightly and adhere to the shell very strongly. In Malaya the general custom is said to be to expose oil palm kernels to the air in layers 4 to 5 feet deep, in roofed sheds equipped with concrete floors.[4] A month's drying under these conditions suffices for reasonably good cracking and separation, and six weeks' drying insures good separation. Some factories use steam-heated drying rooms, in which the nuts, contained on wire trays, are adequately dried in 3 days. Another effective drying method is to treat the nuts with live steam in a revolving drum for 1 to 2 hours, after which they are air-dried for a few hours. Because of their thicker shells, American palm nuts such as the cohune and the babassu would be expected to dry more slowly. Aside from the fact that it is necessary for efficient decortication, thorough drying of the nuts will of course minimize the danger of deterioration in the kernels from enzyme action.

(c) Reduction of Oil Seeds

The extraction of oil from oil seeds, either by mechanical expression or by means of solvents, is facilitated by reduction of the seed to small particles.

Opinion is divided as to whether the grinding or rolling of oil seeds actually disrupts a large proportion of the oil-bearing cells. The assumption of extensive cell breakage has in the past been based chiefly upon the fact that seed flakes yield a large fraction of "easily extractable" oil upon treatment with solvents, and a smaller fraction (usually 10–30%) of oil that is extracted with much greater difficulty.[5,6] The former fraction was presumed to come from broken cells. However, it has recently been shown[7] that seeds (soybeans) that are cracked rather than rolled, with a minimum of crushing, likewise yield a large fraction of oil that is easily washed out with solvents. Furthermore, Woolrich and Carpenter[8] could observe little disruption of cells in rolled cottonseed flakes examined under the microscope. As an argument against extensive cell destruction they pointed out that the cells of cottonseed are but 0.001–0.0015 inch

[4] B. Bunting, C. D. V. Georgi, and J. N. Milsum, *The Oil Palm in Malaya*, Dept. Agr., Straits Settlements and Federated Malay States, Kuala Lumpur, 1934.
[5] A. M. Goldovskii and M. Podol'skaia, *Masloboino Zhirovoe Delo*, *10*, No. 4 (1934).
[6] J. O. Osburn and D. L. Katz, *Trans. Am. Inst. Chem. Engrs.*, *40*, 511–531 (1944).
[7] G. Karnofsky, *Proceedings of a Six-Day Short Course in Vegetable Oils*, American Oil Chemists' Society, University of Illinois, 1948, pp. 61–69.
[8] W. R. Woolrich and E. L. Carpenter, *Mechanical Processing of Cottonseed*, Engineering Expt. Sta., Univ of Tennessee, Knoxville, 1935.

in diameter, whereas the thickness of rolled cottonseed particles is not less than 0.005 inch. On the other hand, Shchepkina's[9] rather high estimates of the proportion of broken cells were made from a count of free aleurone grains in flake samples.

In any event, it appears that many oil cells remain intact after even the most careful reduction, and that the walls of these cells are made
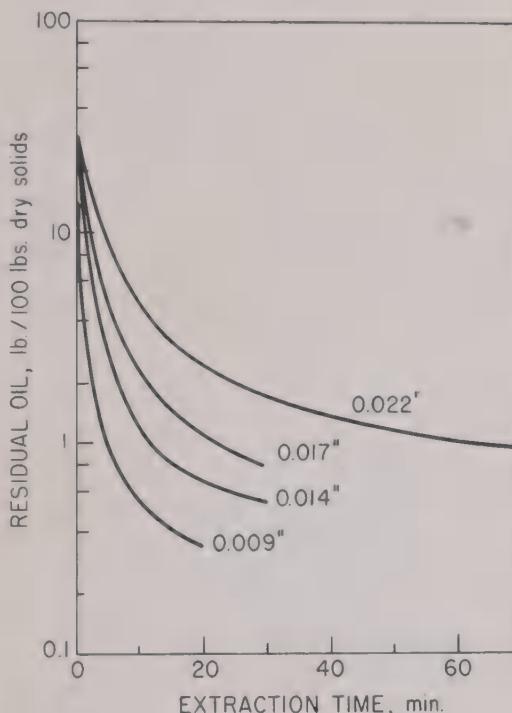
Fig. 63. Relation of flake thickness to extraction rate in the solvent extraction of soybean flakes by percolation with hexane.[7]

permeable to the oil only by the action of heat and moisture in the cooking operation. However, the cell walls will be more readily acted upon by heat and moisture if the seed particles are small.

Obviously, rolling seed or seed particles into thin flakes will facilitate solvent extraction, both from the disruptive effect of rolling and by reducing the distances that solvent and oil must diffuse in and out of the seed during the extraction process. It has been shown that the rate-controlling factor in the solvent extraction of seed flakes is probably the internal resistance of the flakes to the molecular diffusion of solvent and oil.[10] If this is the case, the extraction rate should theoretically be in indirect proportion to the square of the flake thickness (page 583);

[9] O. Shchepkina, *Masloboino Zhirovoe Delo, 10*, No. 4 (1934).
[10] D. F. Boucher, J. C. Brier, and J. O. Osburn, *Trans. Am. Inst. Chem. Engrs.,* *38*, 967–993 (1942).

doubling the thickness, for example, should quadruple the time required for reduction of the residual oil to a given level. The data of Karnofsky[7] on soybean flakes, shown in Figure 63, roughly bear out this expectation. In practice, however, there are other factors to be considered, such as the mechanical strength of the flakes and the resistance offered by the flake mass to the flow of solvent. Consequently, for solvent extraction, seeds are not usually rolled to the least possible thickness.
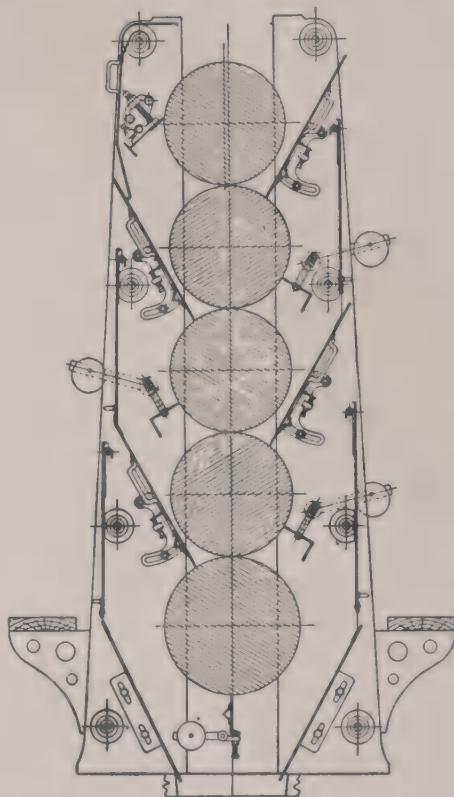
Fig. 64. Five-high crushing rolls, cross section (courtesy *The French Oil Mill Machinery Co.*).

Hammer mills, attrition mills, and other devices are sometimes used for the preliminary reduction of large oil seeds, such as copra and palm or babassu kernels, but for the final reduction of oil seeds it is the almost invariable practice in the United State to use milling rolls. Rolls are generally considered to be more economical to operate than other types of mills. The thin flakes to which oil seeds are reduced by smooth rolls are more satisfactory for hydraulic pressing than the irregularly shaped particles obtained by grinding. Flaking rolls are essential for preparing oil seeds for continuous solvent extraction, since no other form of mill is capable of forming particles which are thin enough to extract readily,

yet large enough and coherent enough to form a mass through which the solvent will freely flow.

The roll assembly commonly used for the reduction of cottonseed, flax-seed, and peanuts in the mills of the southern United States (Fig. 64), consists of a series of five rolls placed one above the other. The seed is introduced, by a feeding mechanism, between the two top rolls. It passes back and forth between adjoining pairs of rolls as it travels from the top to the bottom of the assembly; hence is actually rolled four times. The assembly is so constructed that each roll supports the weight of all of the rolls above it, so that the seed particles are subjected to progressively increasing pressure as they pass from one pair of rolls to another. Although the lower rolls are smooth, the top roll is commonly corrugated, to insure that the seed will be "nipped" as fast as they are fed to it. A popular five-high roll assembly consists of four upper rolls each 14 inches in diam-eter by 48 inches in width, and a bottom roll 16 inches by 48 inches in size, operating at a peripheral speed of about 630 feet per minute. This unit has a rated capacity of 80 short tons of cottonseed or 300 bushels of linseed in 24 hours. However, the actual capacity in any case depends upon the flake thickness that is obtained. Detailed data on the capacity and efficiency of cottonseed flaking rolls have been published by Wamble.[11]

Cottonseed are usually rolled to a thickness of between 0.005 and 0.008 inch. The optimum yield of oil is said to be obtained with flakes of ap-proximately the former thickness.[8] The repeated passage of the material through the rolls results in considerable breaking up of the individual flakes, but this is not particularly disadvantageous in the case of seed which are to be mechanically expressed. Small oil seeds, such as flaxseed and sesame, are usually rolled in preparation for expression.

In the preparation of oil seeds for expression in expellers or screw presses, the production of thin particles is not so essential as for hydraulic pressing, since heat is generated and seed particles are broken up by the intense sheering stresses developed in the barrel of the expeller. Soybeans which are to be processed in expellers are usually cracked into particles averaging 10 to 16 mesh in size, by corrugated cracking rolls, and are then expressed without rolling or further reduction. Palm kernels, copra, peanuts, etc., are handled in expeller plants both with and without rolling. Cottonseed are usually rolled before expression in expellers.

The rolls used for flaking soybeans or other oil seeds for solvent extrac-tion are somewhat different in design from those described above. Since large, coherent flakes are desired for solvent extraction, the flaking opera-tion must be carried out by a single passage of the whole or cracked seeds through the rolls. A single pair of rolls, therefore, is provided; the rolls

[11] A. C. Wamble, Chapter XIV. in *Cottonseed and Cottonseed Products*. A. E. Bailey, ed., Interscience, New York, 1948.

are mounted side by side rather than being superimposed, and are equipped with heavy springs to maintain the pressure of one roll against the other. Since the clearance between rolls of this type is positively adjustable, flakes are produced of quite uniform thickness.

A reasonably high moisture content is required in oil seeds which are to be formed into thin, coherent flakes. Very dry seeds do not flake well. For solvent extraction, cracked soybeans are dried to a moisture content of 8–11% and flaked while still hot and slightly plastic, i.e., while at a temperature of 140–160°F.[8a] In some cases the cracked beans are steamed for a short time prior to flaking.

B. Heat Treatment of Oil-Bearing Materials

The heat treatments given oil-bearing materials may be divided into two categories, according to whether they are alone productive of oil, or merely serve to facilitate the subsequent expression of oil by mechanical means. The term "rendering" is generally applied to treatment designed to remove all or most of the oil from fatty animal tissues or other materials with a high ratio of oil to solid matter. The heat treatment applied to oil seeds and similar materials prior to pressing is more commonly termed "cooking." Some methods of processing are a combination of rendering and cooking.

In the case of either rendering or cooking, the principal object of the heat treatment is the same, i.e., to coagulate the proteins in the walls of the fat-containing cells and make the walls permeable to the flow of oil. The flow of oil from the oil-bearing material is also assisted by the lowered viscosity of the oil at elevated temperatures. Since oil-containing materials are never completely dry, heat treatment is inevitably associated with various effects due to the presence of moisture, even when water is not added in the processing operation. As a matter of fact, it is necessary for water to be present for the above-mentioned protein coagulation to take place. Anhydrous proteins do not readily coagulate or exhibit other evidences of heat denaturation. In some cases water also assists in the displacement of oil from the surfaces of solid materials, through a superior physicochemical affinity for the latter.

1. Rendering of Animal Fats[12]

Fatty animal tissues free from muscle or bone are usually 70–90% fat; the remainder consists of water plus a small amount of connective

[12] For a recent review of rendering, as carried out in meat packing establishments in the U. S., see F. C. Vibrans, *J. Am. Oil Chem. Soc.*, *26*, 575–580 (1949). For a similar review, with emphasis upon European techniques, see M. Maillet, *Inds. corps gras*, *3*, 38–46 (1947).

tissue. The latter is made up largely of proteins, hence the residue from rendering ("tankage," "cracklings," "stick," etc.), like the residue from the processing of oil seeds, is essentially a protein concentrate, which is used principally as an animal feed.

The product of highest fat content obtained in meat packing establishments is leaf fat from hogs, which is 92–95% fat. The internal fat from cattle used for the manufacture of oleo stock contains 60–80% fat. Back fat and other so-called "cutting fat" from pork runs 80–85% fat. A considerable amount of lard and tallow is obtained, however, from bone stock and other low-fat material, which may not contain more than 10–15% fat. Under certain circumstances, whole carcasses of large animals may be rendered for inedible fat recovery and conversion of the residue to tankage. Most of the fish oil produced comes from the rendering of whole small oily fishes such as sardines and herring (which contain 10–20% oil), whereas whales, which give an average oil yield in the neighborhood of 30,000 pounds per animal, are trimmed of their fatty tissues or blubber, which contains ca. 70% fat, and this is rendered separately from bones or flesh.

Methods of rendering are dictated by the nature of the fatty stock, as well as the characteristics desired in the rendered fat and the rendering equipment available.

(a) Dry Rendering

"Dry" rendering is one of the simpler methods of oil extraction. It is distinguished from "wet" rendering by the fact that the expulsion of oil is accompanied by dehydration of the fat and fatty tissues, so that the latter are essentially dry at the end of the operation. The frying of bacon, to cite a familiar example, is essentially a dry-rendering process.

In its simplest form, dry rendering is carried out in an open kettle, which is equipped with a low-pressure steam jacket and a low-speed agitator designed to prevent the fatty tissues from adhering to the heated kettle walls. The kettle may be of any convenient size, but will ordinarily hold several thousand pounds. The well-hashed stock is charged to the kettle without the addition of water, and is heated and stirred until the charge is substantially dry and at a temperature of about 230°F. The dried residue of connective tissues, etc., or "cracklings," is strained from the fat and then pressed in a hydraulic or screw-type press.

In the United States, leaf lard is almost invariably rendered by the "open-kettle" method described above. The quality of lard produced by this method is inclined to depend more upon the care exercised in handling the fatty stock than upon the details of the rendering operation. In order to produce a fat low in free fatty acids, it is particularly important that

the leaf fat be rendered soon after it is removed from the animal. In some establishments it is customary to hang the fat in coolers for an overnight period before it is hashed and rendered. It is preferable, however, to hash and render the warm fat immediately. By this procedure it is possible to produce a lard with a free fatty acid content between 0.10 and 0.15%. Lard rendered by the open-kettle method has a distinctive "cooked" flavor which is preferred by many to the milder flavor of steam-rendered lard. Lard from other fat than leaf fat is occasionally rendered by this method, as are also tallow and other fats, especially in small establishments.

Open-kettle rendering is relatively slow and inefficient, and is not often used for the large-scale rendering of lard or other fats. Manufacturers who prefer to render a large proportion of their fats by the dry method usually conduct the operation in closed tanks which during at least a portion of the rendering period are maintained under reduced pressure. The application of vacuum greatly facilitates the removal of water from the charge, and protects the fat from oxidation. Vacuum dry rendering is usually carried out in horizontal, cylindrical, steam-jacketed vessels equipped with mechanical agitators. A typical batch dry-rendering unit is described by Merkel.[13] Continuous dry-rendering systems have also been devised. A recent United States patent[13a] describes a process wherein the fat is very finely hashed, heated, and discharged into an evacuated chamber to flash off moisture. A fat which is very neutral in flavor and very low in free fatty acids is said to be produced.

Dry-rendered fats contain a small amount of proteinaceous substances, which impart a distinctive flavor, and in some cases a somewhat dark color to the fat. The color may be controlled to some extent by regulating the degree to which the charge is allowed to become dehydrated. These coloring substances are inclined to enter the fat to a serious extent only in the absence of much moisture. They apparently exist in the fat in the form of a colloidal dispersion rather than a true solution, and in some cases may be partially precipitated and removed by hydration, by giving the fat a light alkali treatment, or even a water wash. Because of the tendency of such substances to dissolve or disperse in dry-rendered fats, this method of rendering is usually confined to stock which consists substantially of fatty tissue, with little admixture of muscular tissue, etc. Dry-rendered fats, if prepared from fresh materials, are naturally lower in free fatty acid content than steam-rendered fats, since they are not exposed to the hydrolyzing effect of long contact with steam or water at a high temperature.

[13] A. H. Merkel, *Food Inds.*, 8, 179–180, 210 (1936).
[13a] J. C. Hormel (to Geo. A. Hormel & Co.), U. S. Pat. 2,467,529 (1949).

(b) Wet Rendering

"Wet" rendering is carried out in the presence of a large amount of water; during the operation the separated fat rises to the top of the water and is skimmed off. There are two varieties of wet rendering, viz., low-temperature rendering, which is conducted at temperatures up to the boiling point of water, in open vessels, and high-temperature or steam rendering, which is carried out under pressure, in closed vessels.

Low-temperature wet rendering is employed mainly where it is desired to produce a fat of very neutral flavor. The apparatus used is simple, consisting of an open tank, equipped with a slow-speed agitator and a jacket for steam at near atmospheric pressure. The fatty stock is placed in the tank, water is added, and the contents are heated with gentle stirring, until the greater portion of the fat rises in a layer to the top of the kettle; after clarification with 1.5–2.5% of dry salt it may be drawn off. The temperatures employed by different processors are somewhat variable; however, the blandest fats are obtained by operating at the lowest practicable temperature, which may not be greatly in excess of the melting point of the fat, e.g., 155°F. in the case of oleo stock, or 126°F. in the case of neutral lard. Rendering the stock at a low temperature does not result in a complete recovery of the fat, and it is customary to re-render the residues, with other fatty stock, under steam pressure.

The most important products of low-temperature wet rendering are oleo stock and neutral lard.

Low-temperature wet rendering was formerly a process of great importance, before the techniques of producing neutral vegetable oils were well developed, and this was virtually the only method of obtaining fats suitable for margarine manufacture. Lately the production of low-temperature rendered fats has greatly declined. The manufacture of oleo stock and oleo oil has decreased, and many establishments have discontinued the rendering of neutral lard altogether.

Much the greater part of the animal fat produced in the United States is rendered by the steam process. The lard produced by this method of rendering is known as "prime steam lard." In addition to lard, tallow and whale oil are also usually steam rendered.

The apparatus used in packing houses in the United States consists of a vertical cylindrical steel autoclave or digester, with a cone bottom, designed for a steam pressure of 40 to 60 pounds per square inch and a correspondingly high temperature. The vessel is filled with the fatty material plus a small amount of water, and steam is admitted to boil the water and displace the air. The vessel is then closed except for a small vent, and the injection of steam is continued until the operating temperature and pressure are attained, after which digestion is continued for a vari-

able time, depending upon the temperature and also the nature of the charge. The usual digestion time amounts to 4 to 6 hours. Under the influence of the high temperature employed, the fatty materials in the digester disintegrate to some extent, and there is a very efficient separation of the fat, which rises to the top of the vessel, leaving a layer of solids (tankage) and "stick water" in the bottom. Pressure is then slowly relieved, and the fat–water interface is adjusted to the level of a draw-off cock on the side of the vessel. The fat is drawn off and purified from traces of water and solid material by settling or occasionally by centrifuging. Eventually it may be filtered.

In the steam rendering of high-fat stocks, 99.5% or more of the fat in the raw material is ordinarily recovered. The fat that is not recovered consists of a small residue in the tankage, plus a very small amount which remains in the "stick water." The usual packing house "killing" and "cutting" fats will yield about 80% and 70% lard, respectively, plus 2–3% each of dry tankage and dry "stick" or solid residue from the evaporation of "stick water." The dry tankage and stick will ordinarily contain about 10–12% and 1.5–2% of fat, respectively. Both are high in protein content; tankage from good stock may analyze as high as 70–72% protein, and stick may be as high as 90% or more.

The advantages of steam rendering are that an efficient recovery of fat is obtained in relatively simple equipment, and that it is adaptable to a wide variety of materials. There is little tendency for proteins, etc., to dissolve or disperse in the fat in the presence of water; hence the fatty stock may contain a large proportion of nonfatty tissue. Bony stock can be handled by this process, since it is effectively disintegrated by prolonged treatment with steam under an elevated pressure. Steam rendering is less rapid and less efficient from the standpoint of heat consumption than dry rendering, however, and a large amount of water must be evaporated in order to recover the nonfatty residue in a concentrated form. Some hydrolysis of fat occurs during steam rendering; the free fatty acids content of prime steam lard is seldom less than about 0.35%. At 47 pounds pressure, according to Vibrans,[12] development of free fatty acids is at the rate of about 0.06% per hour. The acidity in any case depends upon the rendering time and temperature and the storage temperature and duration of storage of the fatty stock before it is processed.[12,14] By careful scheduling of operations, killing fats may be rendered reasonably soon after the animals are slaughtered, but carcasses must be chilled for 48–72 hours before cutting fats are available. The stability of lard toward oxidation bears no relation to the acidity, and appears to depend principally upon processing and handling subsequent to rendering.[14]

[14] C. E. Morris, *Oil & Soap, 13,* 60–62 (1936).

Although most steam-rendering systems are of the batch type, they may also be made continuous. The Danish Titan process for lard[15] depends upon fine hashing of the stock and a relatively high temperature and steam pressure (85 p.s.i.g.) to effect very rapid rendering (within about 3 minutes). Following the rendering operation, the solid residue is strained and pressed substantially free of liquids, and the fat is separated from water and finely divided solid material by passage through special high-speed centrifuges built for periodic automatic sludge discharge. If arranged to handle fresh fatty stock, it produces a lard of very high quality which is extremely low in free fatty acids and almost neutral in flavor and odor. It is popular in Europe, but has not yet gained acceptance in the United States, where killing and rendering schedules are less well adapted to a continuous operation, and where efforts to improve the quality of lard have generally taken the direction of refining and deodorizing treatment applied to produce neutral "animal fat shortenings," rather than improvement of the rendering process itself.

A typical unit for the continuous processing of whale blubber has been described by Brocklesby.[2] It consists of feeding sluices, vertical preheating chambers, a horizontal rotary extractor, and a vertical settling tank, all interconnected by automatically operating valves. The hashed blubber is fed into the preheaters, where it is heated with open steam. From the preheaters it is discharged to the extractor, which consists of a horizontal drum, inside of which rotates a slightly smaller perforated drum or strainer. As the charge disintegrates, it gradually works through the strainer, and collects in the bottom of the fixed drum, from which it is pumped to the settling tank. After most of the water and solid material is removed from the fat by settling it is then centrifuged or filtered. Continuous rendering units are said to be gradually replacing other types for the extraction of whale oil.

(c) Digestive Rendering Processes

Considerable attention has been given to wet rendering of animal fats with the assistance of added chemicals or enzymes which promote the separation of fat by hydrolyzing and dissolving the connective tissue.

Deatherage[16] has described in detail laboratory and pilot plant experiments in the alkali rendering of lard and beef fats. The best results were obtained when the fat was digested at 85–95°C. for 45 minutes to an hour with a 1.75% sodium hydroxide solution. After digestion is complete, the fat is separated from the aqueous liquid plus a small amount of undigested solids by centrifuging, and washed, first with 2–5% salt

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[15] See *Natl. Provisioner, 115,* No. 26, 9–10 (Dec. 28, 1946); M. Maillet, *Inds. corps gras, 3,* 38–46 (1947).
[16] F. E. Deatherage, *J. Am. Oil Chem. Soc., 23,* 327–331 (1946); U. S. Pat. 2,456,684 (1948) (to Kroger Grocery & Baking Co.).

solution, and then with water. Fat recovery is equivalent to or better than that obtained by steam rendering, without significant hydrolysis or darkening of the fat or production of the typical cooked flavor of steam lard. The process is best adapted to fat that is reasonably fresh; stocks in which any considerable amount of hydrolysis has occurred are difficult to process because of the excessive formation of soap in the aqueous phase. Soap is derived only from free fatty acids in the fat; under the mild conditions of the digestion there appears to be no appreciable saponification of neutral fat. The fat is, of course, alkali-refined as it is rendered; hence it is produced substantially free of acidity. A typical lard had a free fatty acids content of 0.01% and a Lovibond color of 2 yellow and 0.3 red.

The use of acid or alkali in rendering appears to be particularly desirable in the low-temperature processing of fish livers for the recovery of vitamin oils. Swain[16a] has reported that the presence of 1% of either effects marked improvement in both the recovery of oil and the vitamin A content.

The rendering of vitamin oils on a large scale from cod, tuna, sole, halibut, dogfish, and soupfin shark livers has been described briefly by Granberg.[17] The livers are obtained as a by-product from fish taken for food, and as a primary product from other fish such as the shark. They are collected from widely scattered stations, being shipped in a frozen condition from the more distant points. After being finely ground they are rendered with water containing soda ash, below the boiling temperature. The separated oil is drawn off, washed with centrifugal separation of the wash liquors, dried, apparently with the aid of a chemical drying agent, and filtered. Both livers and oil are bought and sold on the basis of their vitamin A content, which may run 2000 to 2,500,000 units per gram of oil. Most of the fish livers processed for vitamin oil recovery contain 60% or more of oil.[2]

The use of proteolytic enzymes in rendering is described in a number of patents, although it does not appear that the method has been used commercially, except perhaps in the recovery of fish liver oils.[2] The patent of Parfentjev[17a] covers the digestion of fish livers with pepsin at a low pH and a low temperature. The process of Keil[17b] for the recovery of lard or other animal fats involves digestion of the fatty stock with a proteolytic enzyme of vegetable origin, e.g., 0.005–0.020% papain at a pH of 6.0–7.5, followed by heating to 140–185°F. to separate the fat.

[16a] L. A. Swain, *Progress Repts. Pacific Coast Stas. Fisheries Research Board Canada*, No. 58, 3–7 (1944).

[17] W. J. Granberg, *Chem. Inds.*, 65, 41 (1949).

[17a] I. A. Parfentjev, U. S. Pat. 2,395,790 (1946).

[17b] H. L. Keil (to Armour & Co.), U. S. Pat. 2,423,102 (1947).

2. Cooking of Oil Seeds

(a) General Considerations

It is universally recognized that oil seeds yield up their oil more readily to mechanical expression after cooking, but a complete explanation of why this is so is at present lacking. It is certain that the changes brought about by cooking are complex and that they are both chemical and physicochemical in nature.

The oil droplets in a cottonseed or similar oil seed are almost ultra-microscopic in size, and are distributed throughout the seed. One effect of cooking is to cause these very small droplets to coalesce into drops large enough to flow from the seed. An undoubtedly important factor in this phase of the process is the heat denaturation of proteins and similar substances. Before the proteins become coagulated, through denaturation, the oil droplets are virtually in the form of an emulsion. Coagulation causes the emulsion to break, after which there remains only the problem of separating gross droplets of oil from the solid material in the seed. Since the surface of the seed particles is highly extended, surface-activity figures prominently in the displacement of the oil. Cooking, in turn, has a profound influence upon the surface activity of the material. The primary objects of the cooking process may therefore be summarized as follows: (a) to coagulate the proteins in the seed, to permit coalescence of oil droplets and to make the seed permeable to the flow of oil; and (b) to decrease the affinity of the oil for the solid surfaces of the seed, in order that the best possible yield of oil may be obtained when the seed are subsequently pressed.

Important secondary effects of cooking are drying of the seeds to give the seed mass the proper plasticity for efficient pressing, insolubilization of phosphatides and possibly other undesirable impurities, destruction of molds and bacteria, increase of the fluidity of the oil through increase in temperature, and, in the case of cottonseed, detoxification of gossypol or related substances.[18]

One factor which obviously affects the affinity between the seed and the oil, and which is amenable to control in the cooking operation, is the moisture content of the seed. Very dry seeds cannot be efficiently freed of their oil. However, it is impossible to say just how moisture inhibits wetting between the seed and the oil. It may be that the cooking process produces a film of adsorbed liquid water on the seed surfaces, which displaces the oil. On the other hand, the water may be in a more nearly "bound" state, and its presence in the seed in this condition may serve to make the seed surface relatively lipophobic. The optimum moisture of cooked seed varies

[18] O. H. Alderks, Chapter XV, in *Cottonseed and Cottonseed Products*. A. E. Bailey, ed., Interscience, New York, 1948.

widely, according to the variety of the seed and the method to be used for
expression. Thus, for example, the preferred moisture content for soy-
beans which are to be expressed in expellers is but 2–3%. On the other
hand, cottonseed and sunflowerseed are processed in Russian mills, by the
Skipin process[19] at moisture contents as high as 20–21%. The function
of moisture in displacing oil from oil seeds has been particularly empha-
sized by Goldovskii and other Russian writers.[20]

There are many substances in oil seeds which are surface active, such
as phosphatides and free fatty acids, and the degree to which these are
present or become active during cooking doubtless influences the tendency
of the seed to adsorb and retain oil. It is generally observed that damaged
oil seeds give lower yields of oil than undamaged seeds of equivalent oil
content. The tendency of damaged seed to retain oil tenaciously is prob-
ably due to their high content of free fatty acids or other surface-active
agents.

(b) Effect on Quality of Oil and Oilcake

In addition to its effect upon the yield of oil, the method of cooking also
determines to a considerable degree the quality of both the oil and the oil-
cake. Cooking is particularly important in its relation to the refining loss
of the oil. A large part of the oil lost in caustic refining consists of neutral
oil which is emulsified in the foots. Certain surface-active agents naturally
present in the oil favor this emulsification; others appear to inhibit it.[21,22]
The relative proportions of the two classes of substances in the oil depend
to a great extent upon the operation of the cooker. There is little pub-
lished information relative to the identity of the surface-active agents in
crude oils, but it would appear that the substances responsible for high
refining losses are generally phosphatides or related substances. The pres-
ence of gossypol in cottonseed oil is known to contribute to the production
of hard foots and a low refining loss.[22] For the production of cottonseed
oil with a low phosphatide content and a minimum refining loss it is neces-
sary to heat the flaked seed quickly to above 190°F. and then to incorpo-
rate any additional moisture in the form of hot water.[18,23] On the other
hand, the maximum yield of crude oil (high in phosphatide content) is
realized when the temperature is held to 170–180°F. in the first stages of
cooking.[18]

Overcooking of oil seeds is undesirable, as it may produce a dark oil-

[19] A. I. Skipin, Trudy VNIIZh, 40 pp. (Sept., 1935).
[20] A. M. Goldovskii, Fettchem. Umschau, 43, 21–26, 57–64, 84 (1936); Trudy
NIRMMI, No. 1, 64 pp. (1933). A. M. Goldovskii and M. Liubarskaia, Masloboino
Zhirovoe Delo, 11, 586–587 (1935).
[21] J. J. Ganucheau and E. L. D'Aquin, Oil & Soap, 10, 49–50 (1933).
[22] H. D. Royce and F. A. Lindsey, Ind. Eng. Chem., 25, 1047–1050 (1933).
[23] M. K. Thornton, Jr., Oil & Soap, 14, 151–152 (1937).

cake; animal feeders generally prefer a light cake. Also, there is evidence, in the case of cottonseed, at least, that prolonged or drastic cooking may be injurious to the nutritive properties of the cake.[24]   On the other hand, the nutritive value of soybean proteins is definitely improved by moderate cooking; Hayward and co-workers,[25] who were among the first to study this effect, reported an increase in digestibility of 3% and in biological value of 12% upon cooking solvent-extracted seed. The poorer quality of untreated meal is apparently a matter of essential amino acid deficiency with respect to cystine, and more particularly methionine.[26] Ham et al.[27] and Kunitz[28] have established the presence of a heat-labile enzymic inhibitor which interferes with the action of trypsin in rendering methionine available; according to Melnick et al.,[29] there is actually inhibition of the rate of methionine liberation, rather than reduction in total methionine availability.

To improve their palatability and nutritive value, soybean flakes intended for animal feeding are invariably toasted, often in a conventional "stack cooker," before they are shipped from the extraction plant. In any oil seed residue distined to be a source of industrial proteins, cooking is avoided because of the heat denaturation that it causes.

One of the prime purposes of cooking cottonseed is to bring about destruction or deactivation of a principle toxic to certain animals (particularly swine and poultry) which has in the past been generally identified as the complex polyphenolic compound, gossypol. It has recently been shown by Boatner and co-workers[30] that gossypol is associated in the seed with several related compounds, and that one or more of these may actually be responsible for the bulk of the observed toxicity, inasmuch as separated whole pigment glands are much more toxic than purified gossypol.[31]   The toxic principle, whatever it may be, is stable to dry, but not to moist, heat, and is extractable by ethyl ether, acetone, or other polar solvents, but not by petroleum naphtha. Lyman and co-workers,[32] who have made a special study of the cooking of cottonseed in relation to detoxification, recommend that cottonseed meats be brought to a moisture content of at least 14.5% before cooking, that the cooking period

[24] H. S. Olcott and T. D. Fontaine, J. Nutrition, 22, 431–437 (1941); Ind. Eng. Chem., 34, 714–716 (1942).
[25] J. W. Hayward, H. Steenbock, and G. Bohstedt, J. Nutrition, 11, 219–234 (1936).
[26] H. J. Almquist, E. Mecchi, F. H. Kratzer, and C. R. Grau, J. Nutrition, 24, 385–392 (1942). J. W. Hayward and F. H. Hafner, Poultry Sci., 20, 139–150 (1941).
[27] W. E. Ham, R. M. Sandstedt, and F. E. Mussehl, J. Biol. Chem., 161, 635–642 (1945).
[28] M. Kunitz, Science, 101, 668 (1945); J. Gen. Physiol., 29, 149–154 (1946).
[29] D. Melnick, B. L. Oser, and S. Weiss, Science, 103, 326–329 (1946).
[30] See C. H. Boatner, Chapter VI, in Cottonseed and Cottonseed Products, A. E. Bailey, ed., Interscience, New York, 1948.
[31] E. Eagle, L. E. Castillon, C. M. Hall, and C. H. Boatner, Arch. Biochem., 18, 271–277 (1948).
[32] C. M. Lyman, B. R. Holland, and F. Hale, Ind. Eng. Chem., 36, 188–190 (1944).

be at least 90 minutes, and that the final temperature be not less than
115°C. (239°F.). At this high initial moisture content, considerable mois-
ture must, of course, be removed in the later stages of cooking to produce
meats that will press satisfactorily.

(c) Cooking for Hydraulic Pressing

The cooking of oil seeds for hydraulic pressing is usually carried out in
"stack cookers." These (Fig. 65) consist of a series of three to six closed,
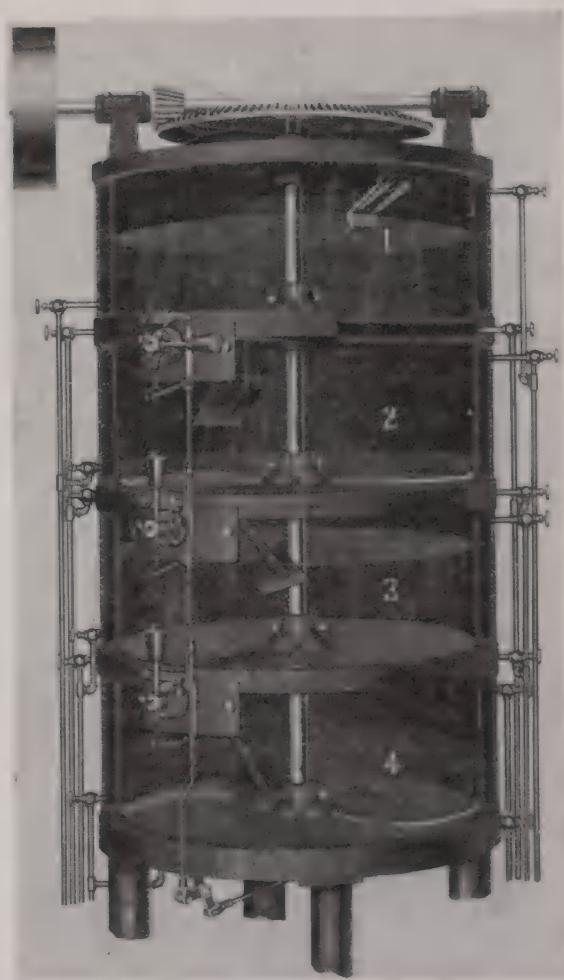
Fig. 65. Phantom view of four-high stack cooker
(courtesy *The French Oil Mill Machinery Co.*).

superimposed cylindrical steel pans, each 2 to 7 feet in diameter and 1.5
to 2.5 feet high. Each pan is independently jacketed for steam heating on
both sides and bottom, and is equipped with a sweep-type stirrer mounted
close to the bottom, and operated by a common shaft extending through

the entire series of pans. There is an automatically operated gate in the bottom of each pan except the last, for discharging the contents to the pan below; the last or bottommost pan feeds into a cake former. The top pan is provided with spray jets, for the addition of moisture to the seed, and each of the lower pans is provided with an exhaust pipe and fan, for the removal of moisture. Thus it is possible to control the moisture of the cooking seed, not only with respect to their final moisture content, but also at each stage of the operation.

In operation, the rolled seed are delivered at a constant rate to the top pan, by means of a conveyor. After a predetermined period of cooking in each pan, each charge of seed is automatically dropped to the previously emptied pan below, so that there is a continuous progression of seed downward through the cooker. The gates which govern the flow of meats from one pan to another may be motor operated, or as is more usually the case, they may be opened and closed automatically by a mechanism which engages the seed at a specific level in each pan. In the latter case, the time that the seed charge remains in each pan is determined by the seed levels for which the pans are set. An 85-inch, five-high cooker, which is a common size, has a rated capacity of 130 tons of cottonseed (calculated upon the basis of the whole seed) per 24 hours.

Steam pressure on the upper stacks of a stack cooker is usually maintained at a relatively high value, e.g., 70 to 90 pounds per square inch, in order to provide quick heating. On the lower stacks it is usually reduced somewhat, since here it is only necessary to maintain the heated seed at cooking temperature. Cottonseed are usually kept in the cooker for 80 to 120 minutes, and are brought out at a temperature of 230–240°F. Seed of good quality are normally cooked larger than poor seed, which are inclined to become dark. Peanuts are often cooked for a somewhat shorter period. Oil seed are usually moistened before cooking, or during the early stages of cooking, unless they are initially fairly high in moisture, and their moisture content is then reduced in the cooker. Alderks[18] recommends a moisture content of 11–12% in the top pan of a 5-high cooker handling cottonseed, and a final moisture content of 5–5.5%. The latter is critical in relation to subsequent pressing of the seed. At lower moisture contents the cake is not sufficiently plastic to deform readily; some plastic flow during expression is essential to efficient expression of the oil. At higher moisture contents, flow occurs too readily, with the result that there is excessive strain on the press cloths, with frequent cloth failures, and large amounts of solid material pass through the cloths into the expressed oil.

A pressure-type cooker for the cooking of cottonseed[33] has found con-

³³ J. Leahy, *Southern Power and Ind.*, *57*, No. 10, 37–44 (1939); R. W. Morton, *Mech. Eng.*, *62*, 731–735 (1940).

siderable favor with some mill operators. This apparatus consists of a horizontal, steam-jacketed cooker, provided with an unheated, vertical holding tank above, and another vertical receiving tank below. The cooker is built to withstand moderate pressure, and is provided with a steam line for the direct injection of steam. Its interior is accurately machined to a cylindrical form, and is provided with a stirrer which operates with a very close clearance (ca. $1/_{32}$ in.) between the stirrer blades and the cylinder walls. The rolled seed are dropped in batches from the holding tank into the cooker and hence into the receiving tank, which discharges to the cake former. Each batch is cooked for 10–20 minutes at about 260–270°F. Pressure cooking not only materially shortens the cooking cycle, but is also claimed to improve the yield and quality of the oil.

A novel cooking method developed by Skipin[19] is said to be in common use in Russian oil mills. This method depends upon the discovery that at a critical temperature, and at a likewise critical and somewhat high moisture content, oil seeds such as cotton, sunflower, and sesame can be made to yield 50% or more of their oil in the cooking pan. The success of the method seems to depend upon the selection of conditions under which there is an extremely selective wetting of the solid seed surfaces by water in preference to oil. Use of the Skipin process does not improve the recovery of oil from the seed, but it is said to increase the capacity of oil mills in which it is used by as much as 50–100%.

In the Skipin process the preliminary separation of oil is obtained in a "forepan," which is similar in construction to a single pan or stack of an ordinary large stack cooker, except that it is equipped with a perforated false bottom. The rolled seed are charged to the forepan, and a sufficient quantity of water is added in the form of a spray to bring the water content of the seed to the optimum level. The moistened mass is then quickly heated with superheated steam to the proper temperature, the heating operation requiring 5 to 6 minutes. It is then maintained at this temperature and slowly stirred, whereupon about half of the oil separates and is drained off through the perforated bottom. During the operation, the residue agglomerates into sizable, plastic lumps. Approximately 30 minutes is allowed for drainage of the oil. After drainage is completed, the somewhat sticky residual lumps are transferred to a "companion pan," and dried until they have lost 2–2.5% of moisture and have become friable. They are then transferred to stack cookers and cooked, dried, and pressed in the usual manner. It is stated that in the processing of sunflower seed it has been possible by means of the Skipin method to increase the turnovers of Anglo-American presses from 2.0 to 2.50 and in some cases 2.75 per hour, without increasing the oil content of the press cake. Cotton-

seed oil extracted in the first stage of the Skipin process is said to have an extremely low refining loss, due to its high content of gossypol.[34]

(d) Cooking for Continuous Pressing

The heat treatment of oil seeds for continuous pressing, by means of screw presses or expellers, is somewhat different from that given seeds which are to be hydraulic pressed. Seed which are to be expeller pressed must be not only cooked, but also dried to a considerable extent, since continuous presses of this type operate satisfactorily only on material of rather low moisture content, usually between 2 and 5%. Cracked soybeans which have been prepared for expeller pressing are usually dried to 2–
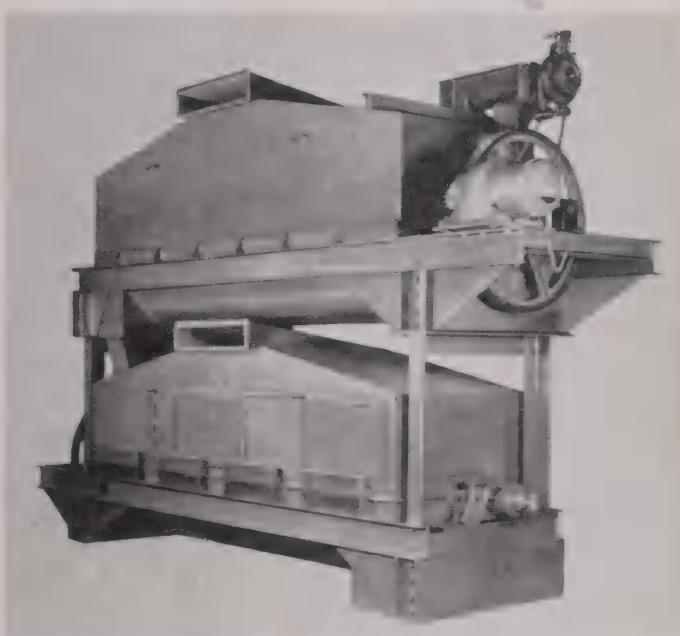
Fig. 66. Soybean dryer (courtesy The V. D. Anderson Co.).

3% moisture by passage through continuous rotary steam-heated dryers, equipped with exhaust fans and dust collectors. In the dryers the beans are brought to a temperature in the neighborhood of 270° F. They are delivered to the expellers at the same temperature, but in order to allow time for protein denaturation and for equilibrium conditions of heat and moisture to be attained throughout the seed particles, they are subjected to an intervening "tempering" period, in steam-heated troughs provided with screw conveyors, which are integral with the expellers or screw presses. The seed experiences a further heat treatment within the expeller

[34] A. I. Skipin and M. Sokolova, Masloboino Zhirovoe Delo, 10, No. 8, 4–11 (1934).

barrel, from heat developed by frictional resistance to their passage. The maximum temperature attained by the seed mass may be well in excess of 300°F. Peanuts are not as yet processed in continuous presses on anything but a very small scale, at least in the United States, but presumably they would require a heat treatment similar to that given soybeans. Copra and babassu kernels are dried and tempered similarly to soybeans.

In the processing of cottonseed and flaxseed the rotary dryers are omitted, and the cooking and drying operation is carried out in a series of continuous, steam-jacketed, horizontal cookers designed to operate under slight steam pressure, which are built directly on the expeller. The seed are rolled before being delivered to the cookers, and are fed to the expeller at a somewhat lower temperature and at a higher moisture content than soybeans.

C. Mechanical Expression of Oil

1. BATCH PRESSING

The oldest and most common method of oil extraction comprises the application of pressure to batches of the oil-bearing material confined in bags, cloths, cages, or other suitable devices.

Levers, wedges, screws, etc., have been used as a means of applying pressure in the more primitive styles of presses, but modern presses are almost invariably actuated by a hydraulic system. Thus the term "hydraulic pressing" is often used in reference to batch pressing in general. There is a limited use of mechanically operated presses for special purposes where a relatively light pressure only is required, for example, in the pressing of partially solidified oleo stock or lard to yield oleo oil or lard oil.

Batch presses may be divided into two main classes, consisting of the "open" type, which requires the oily material to be confined in press cloths, and the "closed" type, which dispenses with press cloths, and confines the material in some species of cage. Open-type presses may be subdivided into plate presses and box presses, and closed-types may be classified as pot presses or cage presses.

The completeness with which the oil is recovered by mechanical expression is influenced by a number of factors related to the affinity of the oil for solid material in the seed. These include the moisture content, the method of cooking, and the chemical composition of the seed; damaged seed generally retain oil more tenaciously than seed of good quality. With a given lot of seed, cooked and ready for pressing, the oil yield will depend upon the rate at which pressure is applied, the maximum pressure attained, the time allowed for oil drainage at full pressure, and the temperature or the viscosity of the oil.

Attempts have been made to establish a correlation between oil recovery from different seeds and the factors of pressure, pressing time, and temperature or viscosity.[35,36] Baskervill and Wamble[36] have shown that, with other factors constant, the fraction, F, of the total oil remain-
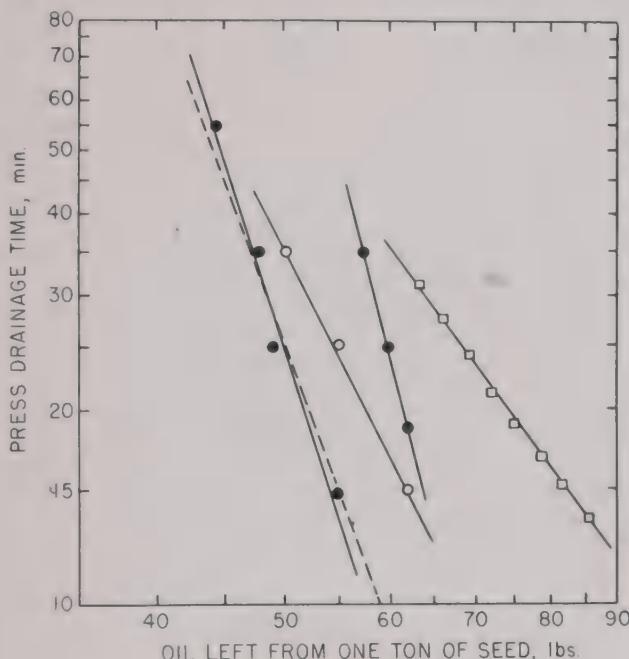
Fig. 67. Relation of press drainage time to residual oil in the hydraulic pressing of cottonseed. Circles represent results in commercial operation; squares represent pilot plant results, according to data of Baskervill and Wamble.[36] Broken line represents approximately a typical press drainage curve, according to Alderks.[18]

ing in rolled, cooked, and hydraulically pressed cottonseed meats at the end of T minutes of pressing time (at maximum pressure) can be expressed approximately by an equation of the form:

$$F = K \, T^n$$

where K is a constant and n is a number less than unity. Ordinarily, the value of n appears to vary from about 0.10 to 0.18, with an average value of perhaps 0.15. The latter value checks with data on the hydraulic pressing of cottonseed oil published later by Alderks.[18]

It follows from the above equation that there is a straight-line relationship between the *logarithm* of the press drainage time and the *logarithm* of the amount of residual oil, expressed either as the fraction

[35] E. C. Koo, *Ind. Eng. Chem.*, *34*, 342–345 (1942). C. F. Gurnham and H. J. Masson, *Ind. Eng. Chem.*, *38*, 1309–1315 (1946).
[36] W. H. Baskervill and A. C. Wamble, *University of Tennessee Expt. Sta. Bull.*, No. 13, 1945.

of total oil or as the pounds of oil left in the cake for a given amount
of seed processed. Representative data from the above sources, in terms
of residual oil per ton of whole cottonseed, are shown in Figure 67. In

practice, the drainage time is, of course,
limited by the necessity for maintaining
reasonable production schedules.
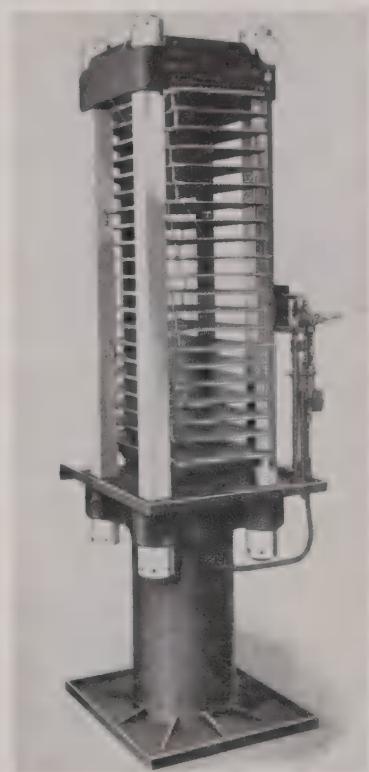
Somewhat scattered data published by
Baskervill and co-workers[37] indicate that
there may be a similar relationship between
the amount of oil left in the cake, with the
fraction of residual oil varying inversely
with about the 0.4 power of the pressure
and the sixth power of the absolute tem-
perature, in degrees Fahrenheit. The con-
siderable effect of temperature is a factor
to be considered in determining optimum
cooking temperatures.

(a) Open-Type Presses

The frame of an open or Anglo-American
press (Fig. 68) consists of four heavy, ver-
tical steel columns fastened at the top and
bottom to heavy end blocks. Within the
open cage formed by the columns, and sus-
pended from the top of the press, are a
series of horizontal steel plates. These plates
closely fill the space enclosed by the

Fig. 68. Plate press (cour-
tesy *The French Oil Mill Ma-
chinery Co.*).

columns. They are equally spaced, at intervals of about 3 to 5 inches, and
are suspended, one from the other, by linkages which permit the entire
assembly to become compressed, in the pressing operation. Below the plate
assembly and attached to a ram operated from below, is a heavier bottom
plate. The material to be pressed is formed into rectangular cakes, which
are placed between the various suspended plates. Raising the ram com-
presses the series of cakes and causes the oil to fall into a drip pan resting
upon the bottom block. The stress created by the application of pressure
is directed against the top block and is translated into longitudinal stress
upon the four columns.

In ordinary plate presses, the oil seed flakes are completely wrapped in
press cloths and placed between the plates without the use of accessory
devices to restrain the cake mass as it is pressed. The surfaces of the
plates, however, are usually either corrugated or covered with hair mats.

[37] W. H. Baskervill, J. A. Glass, and A. H. Morgan, *Oil Mill Gazetteer*, May, 1947.

to assist in the drainage of the oil and to overcome cake creepage. Box presses are provided with a special boxlike arrangement (Fig. 69) which encloses the cake on its two long sides, and simplifies the wrapping of the cake. The complete press box includes a corrugated drainage rack, a perforated and corrugated steel drainage mat which rests upon the drainage rack and underneath the cake, and steel "angles" which project from the underside of each plate to form the sides of the box enclosing the cake below. With this arrangement, it is only necessary for the press cloth to
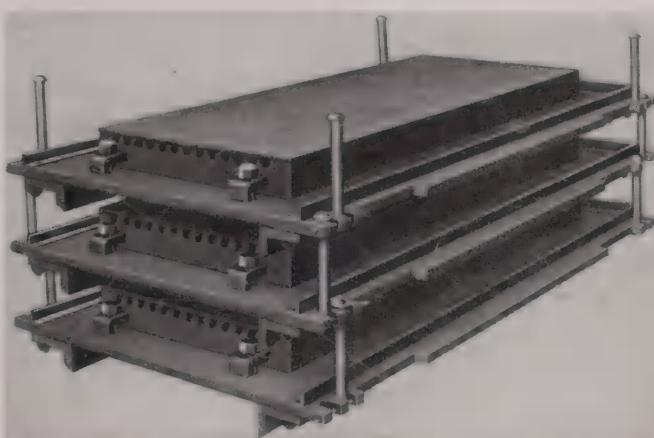
Fig. 69. Press-box assembly, for use in box press (courtesy *The French Oil Mill Machinery Co.*).

enclose the cake on the top, bottom, and ends. Thus, folding of the press cloth in two directions is avoided, and very heavy, durable cloths may be used. Standard size press boxes are about 2 inches deep, and are 35 inches long, 14 inches wide at the back, and $14^3/_8$ inches wide at the front, being slightly widened from back to front to facilitate insertion and removal of the cake. Presses are usually constructed with either 15 or 16 boxes. Plate presses of an equivalent size have 24 plates, and hence have a greater capacity than box presses.

Presses similar to those described above are generally provided with a 16-inch ram operating at a pressure of 4000 to 4500 pounds per square inch, hence the pressure on the cake is between 1650 and 1850 pounds per square inch. It is important to build up pressure upon the cakes gradually. In order to conduct the initial stage of compression more rapidly than the later stages, the hydraulic system operating the presses is provided with automatic valves which deliver oil at 500 pounds pressure to the ram until an equivalent pressure is built up on the cake, and thereafter deliver the maximum pressure of about 4000 pounds. The time allowed for drainage of the oil after the maximum pressure is reached is somewhat variable

among different mill operators. However, a typical press cycle is as follows: for charging the press, 2 minutes; for attaining maximum pressure, 6 minutes; drainage time, 26 minutes; for discharging the press, 2 minutes; total, 36 minutes. The capacity of a 15-box press operated under these conditions is approximately 11 short tons of whole cottonseed or whole peanuts per 24 hours.

According to Baskervill and Wamble,[36] the average press cycle in mills processing cottonseed in the United States is probably 30 minutes or less; their calculations indicate that the economically optimum cycle is approximately 50% longer.

An essential accessory to the operation of either plate or box presses is a cake former for automatically delivering a proper quantity of flakes from the cooker and forming the flakes into a cake of the proper size and shape within the press cloth. Cake formers are designed to press the flakes into a coherent mass without the application of sufficient pressure to start the oil from them. They are hydraulically operated. Mechanically operated cake strippers are also provided for removing the somewhat adherent press cloths from the spent press cake. Charging and discharging the presses is carried out entirely by hand, however. An operator is also required for both the cake former and the cake stripper, as neither is fully automatic.

The edges of the cake coming from an open-type press are soft, and higher in oil content than the remainder of the cake. Consequently, it is the usual practice to slice off or beat off these edges in a mechanical cake trimmer and rework the trimmings through the presses.

Plate presses are usually preferred for flaxseed, whereas box presses are standard equipment in cottonseed or peanut mills. The press cloths used with box presses are woven from human hair, camels' hair, or nylon. A wide variety of materials are used for the cloths used in plate presses, including cotton, wool, hair, etc.

(b) Closed-Type Presses

Cage presses (Figs. 70 and 71) confine the oil-containing materials within a strong perforated steel cage during the pressing operation, and thus largely dispense with the use of press cloths. They may be operated at higher pressures than are practicable with open presses. They are particularly suitable for the expression of copra, palm kernels, and other oil seeds which are high in oil content and low in fiber and hence are inclined to flow and burst the press cloths of open presses. Castor beans or other seeds which it is desired to process without heat treatment can be pressed satisfactorily only in presses of this type, as very high pressures are required to extract the oil efficiently from cold seeds. They are desirable for
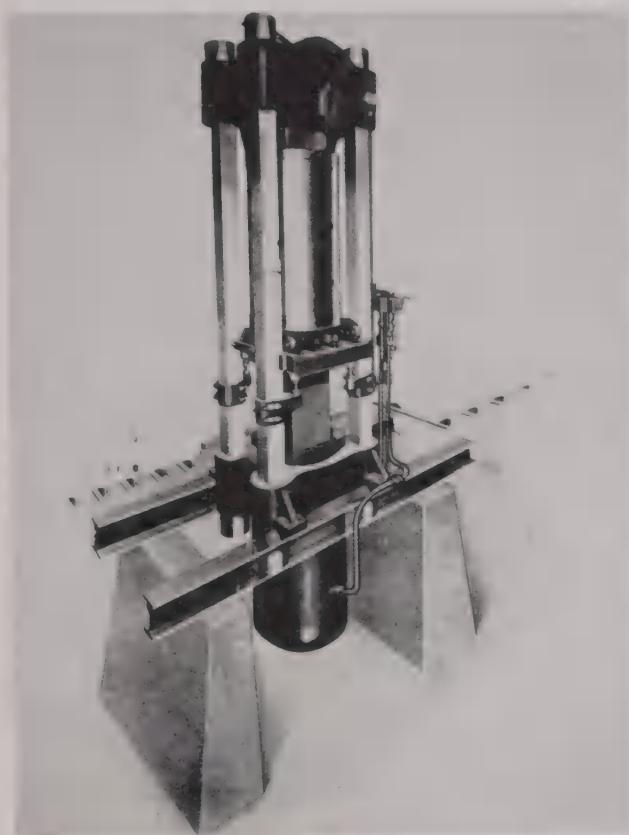
Fig. 70. Cage press (courtesy *The French Oil Mill Machinery Co.*).
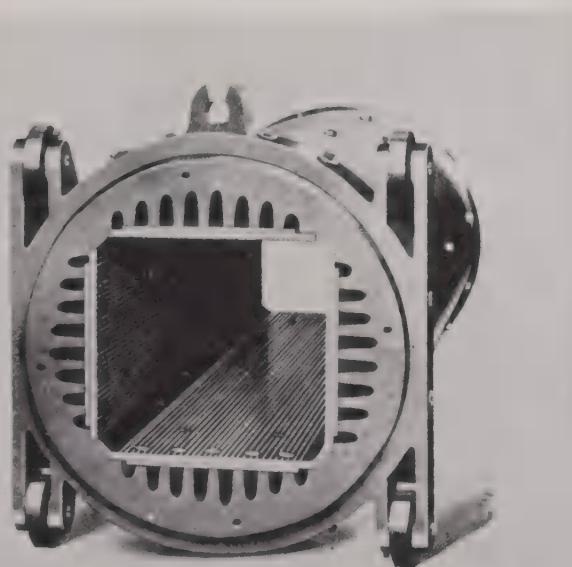
Fig. 71. Square cage from cage press (courtesy *The French Oil Mill Machinery Co.*).

use by mills which process a large number of varieties of oil seeds, as they can be used on practically any oil seed or other oily material.

Cages for this type of press are built in both round and square forms. They are usually made up from a number of closely spaced steel bars or
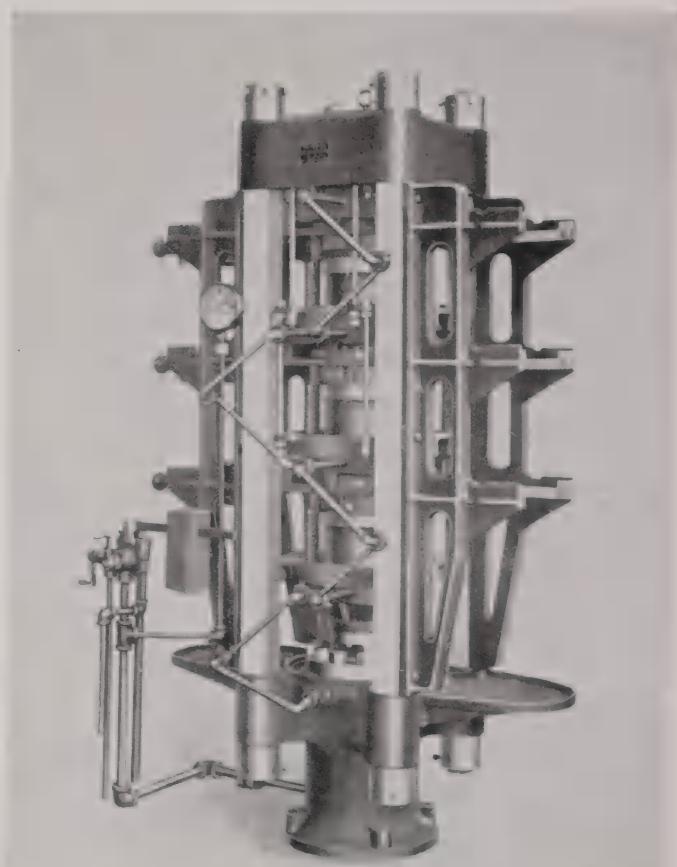
Fig. 72.   Pot press (courtesy *The French Oil Mill Machinery Co.*).

slotted steel plates, supported inside a heavy frame or ringed with heavy steel bands. The channels through which the oil escapes are increased in size from the interior of the cage outward, to minimize any tendency for them to become clogged with solid particles. The cages are operated in a vertical position, in a frame similar to that of the Anglo-American press. Oil is expressed from the charge by forcing a closely fitting head up into the cage from below by means of a hydraulically operated ram. The upper end of the cage may be closed solidly, in which case pressure is applied only to one end of the charge, or the cage may float between the lower ram and an opposed head entering from above. In the latter case, pressure is

applied to both ends of the seed mass. Cage presses are designed to attain pressures of 6000 pounds per square inch, or more.

Since there is a marked tendency for the oil flow in the compressed cake to be longitudinal rather than radial, the cage cannot be packed solidly with the oil seed, but must be charged with layers of seed, which are separated by drainage plates and press cloths. Auxiliary equipment is required for filling the cages and discharging the cake. This, and the rather elaborate and heavy design of the cages, makes the initial cost of this type of pressing equipment relatively high. In large installations the cages are usually made removable from the presses, and filling and discharging presses are provided, in addition to a number of finishing presses. A cage carriage is provided for transferring the heavy cages from one press to another.

The pot press (Fig. 72) is a special form of cage press used for the extraction of cocoa butter or other fats which are solid at ordinary room temperature. In this press the cage is replaced by a series of short, superimposed, steam-heated cylinder sections or "pots." The walls of the pots are solid and drainage takes place through perforated plates and filter mats in the bottom of each section. Pot presses are usually designed for pressures intermediate between those employed in open presses and cage presses, although they can be built for virtually any desired pressure. The advantages of pot presses are that they can be heated and that they can handle very soft, nonfibrous material, such as fruit pulp, at high pressures without forcing large quantities of solid material into the oil. Their capacity is small, however, in relation to their size and cost, and they require more hand labor to operate than other types of presses.

Some oil seeds of high oil content, such as copra, are difficult to express satisfactorily in batch equipment by a single pressing. In some places it is customary to break up the oil cake derived from the first pressing, and subject it to a second pressing, with or without intervening moisture or heat treatment, for the recovery of residual oil. Such practice of course requires a double reduction of the seed, and is also inclined to yield an oil of inferior quality from the second pressing. In American practice, the double pressing of oil seed is generally considered an obsolete method. Oil seeds which cannot be reduced to a low oil content by a single pressing in hydraulic presses are preferably processed in continuous screw presses or expellers.

2. CONTINUOUS PRESSING

Continuous expellers or screw presses are used to the almost complete exclusion of hydraulic presses for the mechanical extraction of soybean

oil in the United States, and are also extensively used throughout the
world for the expression of copra, palm kernels, peanuts, cottonseed, flax-
seed, and almost every other variety of oil seed.

The continuous presses used on oil seeds in the United States are mostly
high-pressure machines which are designed to effect oil recovery in one
step and are usually designed for a particular oil seed. In Europe a
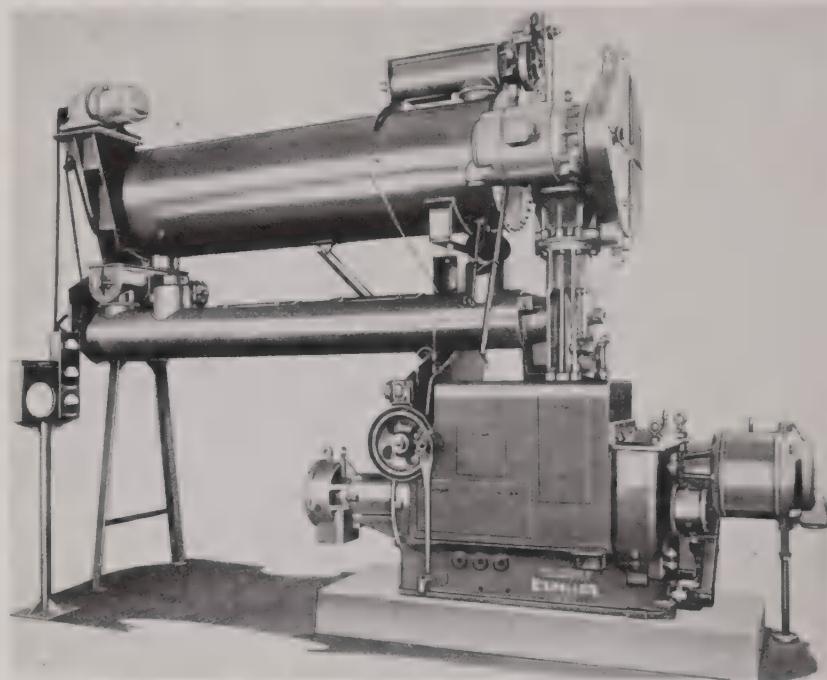
Fig. 73. Modern high-pressure expeller for soybeans (courtesy *The V. D. Anderson
Co.*).

variety of oil seeds is ordinarily handled by the same equipment and it is
common practice to press the seeds in two or even three stages, at in-
creasingly higher pressures in each stage. The low-pressure presses are
also often used for "pre-pressing" of oil seeds prior to solvent extraction.

Continuous presses effect a large saving in common labor over hydraulic
systems, and completely eliminate the need for press cloth. They are
adaptable to a wide variety of materials, and in most cases, they produce
a slightly higher yield of oil than hydraulic presses. Their principal disad-
vantages are that their power requirements are relatively high, they re-
quire fairly well-skilled labor for both operation and maintenance, and
they are not well adapted to intermittent operation.

The screw press is essentially a continuous cage press, in which pressure
is developed by a continuously rotating worm shaft, rather than an inter-

mittently operated ram. An extremely high pressure, of the order of 20,000–40,000 pounds per square inch is built up in the cage or "barrel," through the action of the worm working against an adjustable pressure orifice or choke, which constricts the discharge of cake from the end of the barrel. The interiors of the barrels of these machines are made up of flat steel bars, which are set edgewise around the periphery of the barrel, and are held in place by a heavy cradle-type cage. The openings between the barrel bars, through which the oil must flow, are of the order of 0.005–0.020 inch, and can be adjusted, by changing the thickness of spacers between the bars.

Installations of continuous presses for oil seeds in the United States are practically confined to two makes, which are similar in principle, but slightly different in construction. One of these, the Anderson expeller (Fig. 73), employs a vertical barrel which receives the seed, presses out approximately half the oil, and then passes the partially expressed seed to a larger horizontal barrel, in which additional oil is expressed at a higher pressure. The worms are powered by a 40-h.p. electric gear-reduced motor. To remove the large amount of frictional heat generated, the barrel is cooled while the machine is in operation by passing the expressed oil through a water–oil heat exchanger and then flushing the cooled oil over the exterior of the barrel. The main worm shaft may also be water-cooled, if this is desired. A duplex model is made by the same manufacturer, in which the vertical worm is independently powered by a motor whose speed varies with the load imposed upon it. This arrangement insures a proper coordination of pressing action in the two barrels under wide variations in the character of the seed being pressed, and hence is advantageous if the unit is to be used on a variety of oil seeds. Smaller models are also manufactured, in which the vertical barrel and worm are omitted.

The French screw press has but a single barrel, but the worm is split into two sections, which revolve at different speeds. The first portion of the worm revolves more rapidly than the latter portion and has deeper flights. Thus, its action corresponds to that of the vertical worm of the machine described above. It receives the seed, presses out a portion of the oil at relatively low pressure, and feeds the seed mass to the more slowly revolving screw in the fore part of the barrel, which finishes the pressing operation at an increased pressure. In this machine, cooling of the barrel is obtained by circulation of water through channels in the cage members.

The oil expressed by expellers invariably contains a greater proportion of foots or solid material than hydraulic pressed oil. For the removal of this material, expeller plants are equipped with screening and draining devices which remove the greater portion, and return it to the feed of the machines. The oil is usually given a final filtration in a filter press, to

remove small particles which are not recovered by screening. The removal of meal or foots from the oil is highly necessary, as such material increases the refining loss of the oil out of proportion to its actual amount.

The larger size expellers and screw presses have a 24-hour capacity of 18 to 22 tons of soybeans and 22 to 24 tons of cottonseed (whole seed basis). Their capacities on other oil seeds are copra or babassu kernels, 18 to 20 tons, flaxseed, about 15 tons. In plants processing soybeans, the power requirements are said to be 80–100 k.w.h. per ton of beans processed.[37a]

Freshly pressed soybean expeller cake is both very dry and very hot. It is usually sprinkled with sufficient water as it leaves the expeller to reduce its temperature and increase its moisture content from about 2% to 10–12%. On the basis of a 10% moisture content, the oil content of soybean cake is usually about 4.0–4.5%. In well-operated expeller plants, 43% protein cottonseed cake can consistently be produced with an oil content of 4% or less. Flaxseed cake produced by expellers usually has an oil content of less than 4%.

3. LOW-PRESSURE PRESSING

For the pre-pressing of oil seeds prior to extraction, ordinary high-pressure screw presses may be operated at low pressure and at increased capacity. However, in new installations special low-pressure presses designed specifically for pre-pressing are usually used. One large American plant designed originally for the solvent extraction of cottonseed in one step has recently been converted to combined screw pressing and extraction.[38] A material improvement is said to have resulted in the oil yield, together with a reduction of about 2% in the refining loss of the crude oil.

Expellers and screw presses of the same design as those used for oil seeds are sometimes used for pressing whale or seal flesh or fish, and for processing meat scraps, but these materials are more commonly handled in screw presses which are specially designed for the purpose. These are generally of lighter construction than the machines built for oil seed extraction, and are operated under lower pressure. A modern unit for the recovery of oil from sardines or similar fish, which employs a screw press in connection with a continuous pressure cooker and meal drier, is described by Brocklesby.[14] The extract from such materials consists of a mixture of water and oil, with a small amount of solid matter. The oil must of course be further separated by settling, centrifuging, filtering, etc.

[37a] L. F. Langhurst, Chapter XIV, in *Soybeans and Soybean Products*, K. S. Markley, ed., Interscience, N. Y., 1950.

[38] N. H. Moore, *Cotton Gin & Oil Mill Press, 52*, No. 7, 34–36 (April 1, 1950).

4. Centrifugal Expression

The removal of oil from an oil-bearing material by centrifugation is a standard method only in the case of palm fruit. The centrifugal recovery of palm oil will be discussed in a later part of this chapter.

D. Solvent Extraction

1. Application

While extraction with solvents constitutes the most efficient method for the recovery of oil from any oil-bearing material, it is relatively most advantageous in the processing of seeds or other material low in oil.

The minimum oil content to which oilcake can be reduced by mechanical expression is approximately the same for all oil seeds, *i.e.*, about 4–5%.

Table 105

Comparison of Solvent Extraction and the Most Efficient Mechanical Expression, as Applied to Oil Seeds of Low, Medium, and High Oil Content

	Soybeans	Cottonseed	Peanuts
Oilseed	Low	Medium	High
Oil content			
Composition of flaked seed, lbs./100 lbs. seed:			
Oil	18.6	32.5	50.0
Solids	69.0	60.0	44.0
Moisture	12.4	7.5	6.0
Yields from processing, lbs./100 lbs. flaked seeds:.			
Mechanical expression:			
Oil...Oil	15.0	29.8	48.0
Cake or meal...Oil	3.6	2.7	2.0
Solids	69.0	60.0	44.0
Moisture	9.0	5.0	4.0
Per cent oil in cake	4.4	4.1	4.0
Per cent total oil recovered	80.6	91.7	96.0
Solvent extraction:			
Oil...Oil	18.0	32.0	49.65
Cake or meal...Oil	0.6	0.5	0.35
Solids	69.0	60.0	44.0
Moisture	9.0	5.0	4.0
Per cent oil in cake	0.76	0.76	0.72
Per cent total oil recovered	96.7	98.5	99.3
Comparison of yields:			
Yield by mechanical expression, lbs. oil/100 lbs. flaked seed	15.0	29.8	48.0
Yield by solvent extraction, lbs. oil/100 lbs. flaked seed	18.0	32.0	49.65
Increase by solvent extraction, lbs.	3.0	2.2	1.65
Increase by solvent extraction, %	20.0	7.4	3.4

Consequently, the oil unrecoverable by mechanical expression, in terms
of percentage of the total oil, increases progressively as the oil content of
the seed decreases. Comparative yields of oil from representative seeds of
low, medium, and high oil content by the two methods of processing, are
shown approximately in Table 105. It will be seen that the substitution of
solvent extraction for pressing methods may increase the yield of oil from
soybeans by 20%, whereas in the processing of cottonseed the increase
may be only about 7%, and in the case of peanuts it may be but 3%.
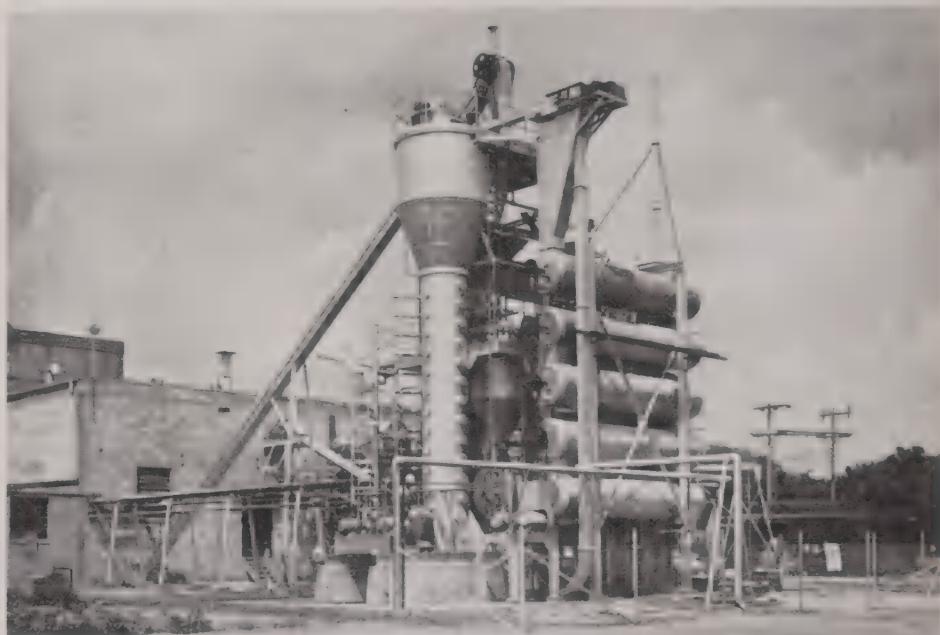
Fig. 74.   Modern medium-size soybean oil extraction plant
(courtesy *The V. D. Anderson Co.*).

In some cases the application of solvent extraction to specific oil seeds
is limited by mechanical considerations. The most efficient extraction is
obtained only in continuous countercurrent systems, in which the solvent
and the seeds make contact with each other in streams moving continu-
ously in opposite directions. Most of these systems can be operated satis-
factorily only if the seed flakes substantially retain their original form
during extraction. If the flakes are inclined to disintegrate under the in-
fluence of the solvent, the fine particles will not only be difficult to sepa-
rate from the miscella, or solvent–oil mixture, but will also impede its
uniform circulation through the seed mass.

The operator of the extraction plant will then be faced with the alterna-
tive of resorting to troublesome and expensive methods of removing a
large amount of fines from the miscella, or operating the plant at a greatly

reduced capacity. In general, the mechanical strength of flaked oil seeds is in direct proportion to the content of solid material, and hence indirectly proportional to the oil content. For this reason, the extraction of low-oil seeds is mechanically simpler, as well as economically more advantageous.

Of all the common oil seeds, soybeans are solvent extracted most easily. In the crop year 1948–1949 it was estimated by the Production and Marketing Administration of the United States Department of Agriculture that 39.6% of the soybeans processed were solvent extracted, with an average yield of 10.94 pounds of oil per bushel, as compared with 55.3% screw pressed, with an oil yield of 9.16 pounds of oil per bushel, and 5.1% hydraulic pressed, with an 8.67 pound oil yield. Cottonseed flakes disintegrate more readily, and occasion more trouble from the production of fines, whereas peanuts and flaxseed disintegrate very badly. By "pre-pressing" or "forepressing" the seed in low-pressure screw presses to remove a portion of the oil it is possible subsequently to solvent-extract high-oil seeds that are difficult or impossible to handle in conventional equipment in their original form. In Europe and elsewhere where European practices have prevailed, it is the general practice to extract whole soybeans, but to pre-press other oil seeds. In the United States pre-pressing is regarded with less favor. It has been avoided in a number of plants recently built for the processing of cottonseed in favor of relatively elaborate systems for the removal and washing of fines from the miscella.

Solvent extraction finds some use in the recovery of animal fats. The tankage or cracklings from dry rendering are often solvent extracted, usually in batch extractors. The recovery of fat from garbage is often carried out by means of solvent extraction, since the low fat content of this material makes other methods of recovery difficult. Garbage is extracted in batch equipment of special design.

Materials containing oil that is scarce or expensive are often solvent extracted, even when the operation is relatively difficult. Examples of materials in this class are castor oil, olive oil, and wheat germ oil residues from mechanical pressing. Solvent extraction may be resorted to to obtain a fat-free residue, or a residue in which proteins are not heat denatured, rather than for the primary purpose of improving the yield of oil. Thus, for example, cocoa is solvent extracted in order to produce a residue which may serve as a source of theobromine. Solvent-extracted meal is preferred for the manufacture of protein adhesives, fibers, or plastics, since there is much less denaturation of the protein in this meal than in that obtained by cooking and mechanical pressing.

In addition to producing a higher yield of oil, solvent extraction has the advantage over mechanical expression of being an almost entirely automatic operation for which labor costs are very low. It has the disad-

vantage of requiring relatively expensive equipment, of being most economical only in comparatively large installations, and of not being well adapted at present to all oil seeds.

2. PRINCIPLES AND THEORY

(a) Methods of Achieving Contact with Solvent

The laboratory extraction of an oil material in an ordinary Butt extraction tube is an example of solvent extraction in its simplest form. In this method of extraction, the pure solvent is delivered continuously to the top of the mass of material to be extracted, and is percolated through the mass by gravity, until the removal of oil is substantially complete. While this method is effective in the laboratory, it is highly inefficient. Complete extraction can be accomplished only by the use of a large volume of solvent relative to the volume of oil extracted. This solvent must eventually be recovered from the oil. Even in the most efficient extraction plants, charges for steam and water for solvent recovery constitute a substantial part of the operating costs,[38a] and if the ratio of solvent to oil is high, such charges may easily become prohibitive. A prime object in modern solvent extraction practice is to reduce the solvent content of the final miscella or oil–solvent mixture to the lowest possible figure. In the best continuous extraction plants the solvent–oil ratio may be as low as 1 to 1 by weight, whereas by simple percolation an equivalent extraction could hardly be accomplished with several times as much solvent.

Some improvement in efficiency is obtained if the continuous percolation of fresh solvent, as described above, is replaced by prolonged treatment of the oil seeds or other material with successive portions of solvent. Each portion is recirculated through the material being extracted until equilibrium or near equilibrium is established between the oil content of the solid material and that of the solvent, i.e., until the free miscella is as rich in oil as the miscella absorbed within the solid particles. When this condition is attained, the free miscella is drained off, a fresh batch of solvent is brought into the system, and the operation is repeated. Extraction is thus continued, in successive cycles of recirculation and drainage, until the oil content of the material is reduced to the value desired.

While batch extraction by means of percolation is satisfactory for some materials, it is not generally adaptable to the large-scale processing of oil seeds. It is virtually impossible to charge large extraction chambers with oil seed flakes without uneven compacting of the material and consequent channelling and incomplete extraction. Hence batch extractors for oil seeds are generally provided with some means of mechanically mixing the solvent and the seed particles. However, from the standpoint of efficiency

[38a] C. W. Bilbe, Mech. Eng., 63, 357–360 (1941).

in maintaining a low solvent–oil ratio it is immaterial whether the solvent and the oil seeds are brought into equilibrium with respect to oil content by circulating the solvent through the seeds while the latter are contained in a tower, or by simply intermixing the solvent and seeds in a chamber of suitable design. The system of extraction by means of successive batches of pure solvent is generally referred to as "multiple extraction."

The last portions of miscella recovered in the multiple extraction process will naturally be very lean in oil. Hence these portions may well be substituted for fresh solvent in the initial treatments of fresh seed. In this way, each portion of solvent is made to perform a double duty, and the amount of solvent to be recovered eventually from the oil is decreased accordingly. A batch extraction system set up in such a manner as to utilize the principle of solvent re-use to the best possible advantage is designated as a "batch countercurrent system." In this system, a battery of extractors is provided, and the solvent is used to treat the contents of each extractor in succession. Each time that a batch of miscella is drained from an extractor it is used to treat a batch of seeds which have previously been extracted with a richer miscella. On the other hand, the drained seeds are each time extracted with a leaner miscella. Thus the seeds are treated with batches of solvent of progressively decreasing oil content until they are finally extracted with fresh solvent and discharged, while the solvent is brought into contact with batches of seed of progressively increasing oil content until it finally encounters fresh seed and is then discharged as the finished miscella. In this way, the miscella is brought out of the system at a uniformly high oil content. If there are a large number of extractors in the battery, the effect approximates that of mixing the solvent and oil in continuously moving countercurrent streams.

Although batch countercurrent extraction may theoretically be brought to an efficiency approaching that of continuous countercurrent extraction, by sufficiently increasing the number of extractors, the system thereby becomes very involved. In practice, therefore, solvent extraction is carried out on the largest scale only in continuous systems, which are entirely automatic in operation. Such systems achieve the highest economy of steam, power, labor, and materials. Their adaptability is limited only by the mechanical difficulties involved in moving the seed mass and the miscella in opposite directions with free intermixing, and in effecting a final separation of the miscella and the seed particles.

If it is assumed in batch extraction that a constant volume of miscella is retained by the seeds after each drainage period, and this volume is known, it is easy to calculate the number of extractions required to reduce the oil content of the seeds to any given level,[39] in the case of either

[39] L. F. Hawley, *J. Ind. Eng. Chem.*, *9*, 866–871 (1917). L. Silberstein, *Ind. Eng. Chem.*, *20*, 899–901 (1938). S. D. Turner, *ibid.*, *21*, 190 (1929).

multiple or batch countercurrent extraction. Actually, however, the retention of miscella is not usually constant, but is variable for different solvent–oil ratios, presumably because of the effect on drainage of such factors as viscosity and surface tension of the miscella. This circumstance renders calculations highly involved, but Ravenscroft[40] has introduced a graphical method for estimating the number of extractions required for a given recovery of oil which is applicable in the case of variable oil retention. Ravenscroft assumes that miscella is retained only on the surface of the solid particles, and refers to this retention as "entrainment." However, his treatment is equally valid for miscella absorbed within the particles, so long as there is equilibrium between the miscella within the particles and without. In the case of continuous countercurrent extraction, differences in oil concentration in the miscella within and without the seed cannot be ignored, since here equilibrium conditions do not exist. Equations for extraction under conditions of nonequilibrium have been developed by Ruth[40a] and by Grosberg.[40b]

(b) Extraction Rates

In practice, the design of large-scale solvent extraction apparatus must be determined by the rate at which equilibrium is attained between a lean miscella outside the seed particles and oil and solvent within the particles. The attainment of equilibrium may be quite slow, particularly as the oil content of the seed (on a dry, solvent-free basis) falls toward the low level (usually below 1.0%) demanded by efficient commercial operation. Modern investigations indicate that the rate at which equilibrium is approached (and hence, in effect the extraction rate) is influenced by a number of factors. These include the intrinsic capacity for diffusion of solvent and oil, which is determined primarily by the viscosities of the two; the size and shape of the seed particles; their internal structure; and, at low seed oil levels, the rate at which the solvent dissolves nonglyceride substances which are oil soluble, but which dissolve less readily than the glyceride portion of the oil.

In a homogeneous oil-impregnated material consisting of thin platelets of uniform thickness whose total surface area is substantially that of the two faces, the theoretical extraction rate, based upon simple diffusion, has been given by Boucher and co-workers[10] as follows:

$$E = \frac{8}{\pi^2} \sum_{n=0}^{n=\infty} \frac{1}{(2n+1)^2} e^{-(2n+1)^2(\pi/2)^2(D\theta/R^2)}$$

[40] E. A. Ravenscroft, *Ind. Eng. Chem.*, 28, 851–855 (1936).
[40a] B. F. Ruth, *Chem. Eng. Progress*, 44, 71–80 (1948).
[40b] J. A. Grosberg, *Ind. Eng. Chem.*, 42, 154–161 (1950).

where E is the fraction of the total oil unextracted at the end of time, θ, in hours; R is one-half the plate thickness, in feet; and D is the diffusion
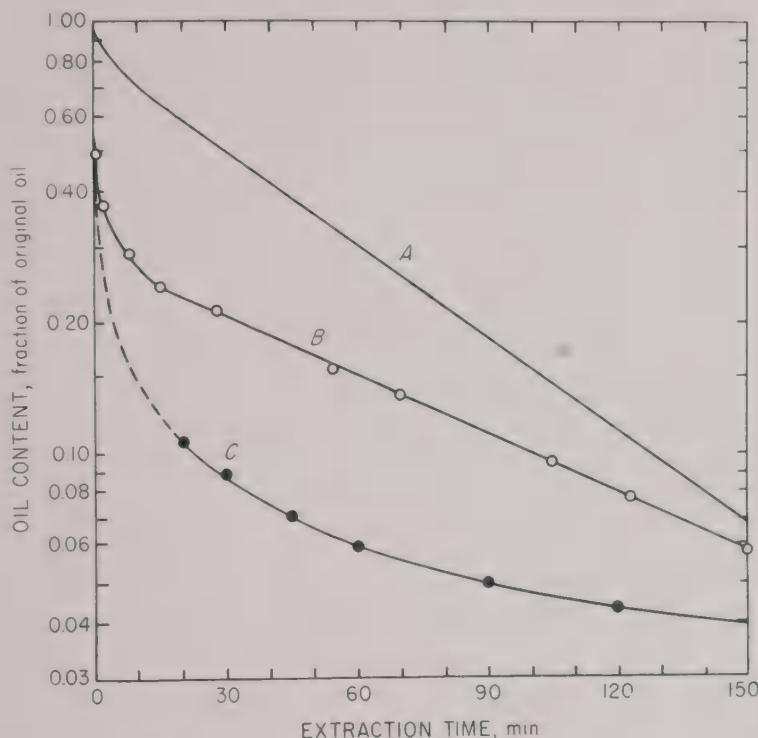
Fig. 75. Solvent extraction curves: (A) theoretical curve for homogeneous oil-impregnated platelets of uniform thickness[10]; (B) peanut slices, 0.026 inch thick, 14% moisture content, extracted at 25°C. with commercial hexane[41]; (C) cottonseed flakes, 0.017 inch thick, 10–25 mesh, 11.6% moisture content, extracted at 150°F. with commercial hexane.[43]

coefficient, in square feet per hour. Except at low values of θ, the above equation takes the approximate form:[41]

$$E = \frac{8}{\pi^2} e^{-\pi^2 D\theta/4R^2}$$

or:

$$\log_{10} E = -0.091 - 1.07 \, (D\theta/R^2)$$

hence at the lower values of E, a plot of $\log E$ against θ gives a straight line with a slope dependent upon the diffusion coefficient and the plate thickness. It is to be emphasized that the equation is valid only when all platelets have the same thickness; an average plate thickness cannot be used for a material of nonuniform thickness.

[41] H. P. Fan, J. C. Morris, and H. Wakeham, *Ind. Eng. Chem.*, *40*, 195–199 (1948).

Working with porous clay plates impregnated with phosphatide-free soybean oil and with tetrachloroethylene as a solvent, Boucher et al. found that experimentally determined extraction rates checked closely with theory; a typical theoretical extraction curve is shown (Curve A) in Figure 75. A lack of correspondence between extraction rates and Reynolds number of the flowing solvent, over a wide range of the latter, indicated that liquid-film resistance to the transfer of oil to the solvent was inconsequential as compared to resistance to diffusion within the plates. The diffusion coefficient was found to be simply a function of the product of the viscosities of solvent and oil; under the particular conditions of their tests it could be represented by the formula:

$$D = 12.96 \times 10^{-6} (\mu_o \mu_s)^{-0.46}$$

where μ_o and μ_s refer to the viscosities, in centipoises, of oil and solvent, respectively. The numerical values in the formula are undoubtedly related to the structure of the plates, and hence can be considered specific only for the lot of plates used in the tests. Tests involving extraction with solvent–oil mixtures as well as pure solvents showed that the diffusion coefficient was independent of the composition of the solvent, in terms of relative proportions of solvent and oil. It can, of course, be expected to increase with increase in temperature, or with use of a less viscous solvent than tetrachloroethylene.

The experiments of Fan and co-workers[41] with peanuts carefully sliced with a microtome show that the relationships developed by Boucher et al. are also applicable to at least one oil seed, provided that structural considerations are not complicated by crushing of the seed to form flakes. A typical extraction curve is shown as Curve B of Figure 75. As required by diffusion theory, there is a linear relationship between the logarithm of the residual oil content and extraction time after a short period has elapsed. However, during this period a large proportion of the oil was extracted very rapidly. Fan et al. carried out a mathematical analysis which indicated that this deviation from theory with respect to rapidly extractable oil was caused by the opening of a certain number of oil-bearing cells in slicing the oil seeds, plus the occurrence of void spaces in the seeds after drying. Thus, they agreed with Osburn and Katz[42] that the major obstacle to extraction is probably diffusion through the cell walls and that the initial rapid extraction is to be attributed to cell destruction. The proportion of easily extractable oil was found to decrease rapidly with increase in the slice thickness. In the case of Curve B of Figure 75, which represents the extraction of peanut slices 0.026 inch thick, the extraction curve became linear after about 76% of the oil was

[42] J. O. Osburn and D. L. Katz, Trans. Am. Inst. Chem. Engrs., 40, 511–531 (1944).

extracted; in other experiments with flakes of similar moisture content, there was linearity with 0.032-inch flakes after about 51% of the oil was extracted, and linearity with 0.040-inch flakes after about 30% was extracted. With flakes of constant thickness, there was a progressive decrease in the content of rapidly extractable oil with increase in the moisture content.
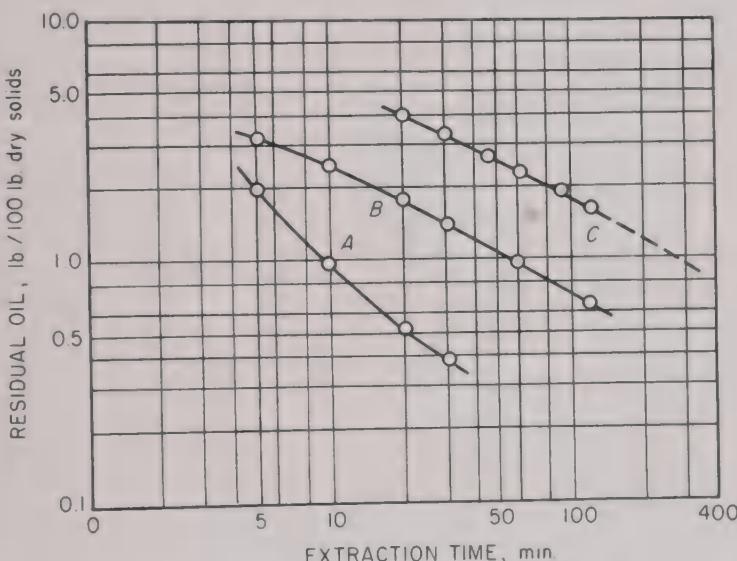
Fig. 76. Representative curves representing laboratory solvent extraction of: (A) soybean flakes, (B) flaxseed flakes, and (C) cottonseed flakes.[43] (Note: Flakes are not necessarily all of the same thickness; hence extraction rates are not comparable.)

Fan and co-workers found that the diffusion coefficient decreased considerably with increase in the moisture content (in the range of 10–22% moisture, about 0.4 square centimeter per second per 1% moisture). With commercial hexane (Skellysolve B) at 24–26°C. and peanut slices with 13% moisture, the calculated diffusion coefficients averaged about 7×10^{-9} square centimeter per second.

In the extraction of oil seed flakes formed commercially by rolling, there appear to be factors which still further complicate the extraction rate. Extraction curves not only reveal a very large fraction of easily extractable oil, but tend to be continuously concave upward from the time axis; Curve C of Figure 75, constructed from the laboratory data of Wingard and Shand,[43] is typical (compare also Figure 63). In practice, extraction in the range of about 5.0–0.5% residual oil (on the basis of the dry, solvent-free meal) is so slow that it actually controls the over-all extraction rate and extractor design.[7] On a semilog plot, the concavity of the extraction curve is so great in this region that, actually, a nearer

[43] M. R. Wingard and W. C. Shand, J. Am. Oil Chem. Soc., 26, 422–426 (1949).

approximation to a straight line is obtained with a log-log plot, as in Figure 76.[43]

A variety of explanations can be offered for the large deviation of Curve C (Fig. 75) from the form of Curve A or Curve B. It has been pointed out by King et al.,[44] as well as by Osburn and Katz,[42] that structural heterogeneity leading to the simultaneous operation of two different diffusion processes with different diffusion coefficients could account for the shape of the curves. The analysis of soybean flake extraction curves by the latter authors suggested that at 80°F. 70–90% of the oil was extracted with trichloroethylene with the relatively high diffusion coefficient of about 4×10^{-6} square foot per hour, while the remaining 10–30% was extracted with the lower diffusion coefficient of about 5×10^{-7} square foot per hour. It was further suggested that the larger portion of readily available oil was derived from cells ruptured in rolling, whereas the smaller portion of difficultly extractable oil was in cells that remained intact. It seems unlikely, however, that such extensive cell destruction could occur (see page 548); if lack of structural homogeneity is the proper explanation, it appears that it is probably of a different kind. Other kinds of heterogeneity can be conceived, including nonuniformity of flake thickness.

As a result of extensive experimental work in the extraction of oil seed flakes, Karnofsky and co-workers[7,44a] have advanced the hypothesis that the slow final extraction rate is at least in part the result of decreased solubility of the last portions of oil. It is well known that oil seeds subjected to repeated extraction with a solvent yield fractions of oil toward the end of the process that are much higher in phosphatides and other nonglyceride materials than the first fractions[7,45]; hence these materials obviously are less soluble. That the difficulty of extracting the last portions of oil from oil seeds may be related to the chemical composition of the "oil" was suggested previously by Goss.[46] Their hypothesis is supported by the observation[44a] that the last portions of oil are removed much more readily if the oil seeds are first given a "soaking" period, even in relatively strong miscella, and that no difficulty is encountered in recovering the last portions of oil from oil seeds reconstituted from extracted oil and oil-free residue.

It should be mentioned that acceptance of the "difficultly soluble oil" theory does not vitiate many of the basic conclusions to be derived from the above theories based upon simple diffusion with free miscibility of solvent and oil. If free miscibility does not exist in the latter stages of ex-

[44] C. O. King, D. L. Katz, and J. C. Brier, Trans. Am. Inst. Chem. Engrs., 40, 533–556 (1944).
[44a] H. B. Coats and G. Karnofsky, J. Am. Oil Chem. Soc., 27, 51–53 (1950).
[45] W. C. Bull and T. H. Hopper, Oil & Soap, 18, 219–222 (1941).
[46] W. H. Goss, Oil & Soap, 23, 348–354 (1946).

traction, this means simply that the effective concentration of solute is not the concentration of "oil" in the solid seed material, but a lower concentration which is limited by the solubility of the "oil" in the solvent. The rate of diffusion will be less than observed in the earlier stages, not because the diffusion coefficient has decreased, but because the "oil" content of the solid material is no longer a proper measure of its instantaneous content of diffusible material. The diffusion or extraction rate will, for example, still be inversely proportional to the square of the flake thickness.

It may be noted that with simple diffusion an increase in the extraction temperature can be expected to increase the extraction rate by lowering the viscosities of solvent and oil, but that with incomplete solubility of the oil an additional effect can be anticipated, through an increase in the solubility. This may account for the great effect of temperature observed by Karnofsky[7]; in one case increasing the temperature from 100°F. to 192°F. reduced by 80% the time required to lower the oil content of cottonseed flakes to 3% with heptane. This is a rather greater effect than would be predicted from a simple decrease in viscosity, according to the data of Boucher et al.[10]

According to Wingard and Phillips,[46a] the time required to reduce oilseeds to 1% residual oil content varies with a power of the temperature which with cottonseed, soybean, and flaxseed flakes and hexane as a solvent, ranged from −1.9 to −2.4. Hence, a plot of log time vs. log temperature yields a straight line.

It is evident in commercial practice, and has been confirmed by closely controlled laboratory experiments, that different oil seeds differ markedly in the rate at which flakes of a given thickness can be extracted to a low residual oil content. The relation of particle size of the oil seed to extraction rate has been clarified by a recent laboratory investigation reported by Coats and Wingard,[46b] who found that the hexane extraction of soybeans, cottonseed, flaxseed, and peanuts, as either flakes or cracked particles (grits), conformed to the mathematical formula:

$$T = K D^n$$

where T = time to reduce the material to a residual oil content of 1.0% (on a dry, solvent-free basis), D = flake thickness or grit diameter, and K and n = constants. Consequently a plot of T against D on a log-log scale yields a straight line, with a slope equal to n. Approximate values found for n were: for four samples of soybean flakes, 2.3 to 2.5; for two samples of cottonseed flakes, 1.5; for one sample of flaxseed flakes, 7; for one sample of peanut flakes, 3.2; for two samples of soybean grits, 5.5; for

[46a] M. R. Wingard and R. C. Phillips, Abstracts of Papers, 41st Annual Meeting of American Oil Chemists' Society, May 1–3, 1950.
[46b] H. B. Coats and M. R. Wingard, J. Am. Oil Chem. Soc., 27, 93–96 (1950).

one sample of cottonseed grits, 4; and for one sample of corn germ grits, 3.4. With T expressed in minutes and D expressed in units of 0.010 inch each, approximate values for K were: for soybean flakes, 6 to 20; for cottonseed flakes, 140 and 270; for flaxseed flakes, 3600; for peanut flakes, 1.4; for soybean grits, 2.5, and 10; cottonseed grits, 40; and for corn germ grits 1.6.

Attention may be called to the fact that K in the above equation is a measure of the ease of extraction (of flakes 0.010 inch thick), whereas n is a measure of the influence of flake thickness upon the extraction rate. Thus, for example, soybean flakes extract more readily than cottonseed flakes of equivalent thickness, and cottonseed flakes, in turn, extract more readily than flaxseed flakes (Fig. 77). The extraction rate of flaxseed is
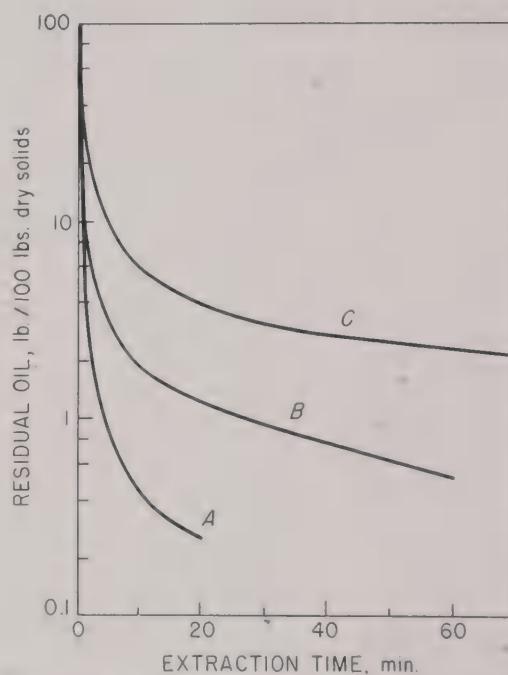
Fig. 77. Relative extraction rates of different oilseed flakes: (A) soybeans, 0.0075 inch thick; (B) cottonseed, 0.0095 inch thick; (C) flaxseed, 0.0075 inch thick.[7]

very highly sensitive to flake or particle thickness, whereas that of soybeans is less so, and cottonseed are less sensitive to flake thickness than either. Soybean grits of a given diameter extract more easily than flakes of equivalent thickness, but their extraction rate is more dependent upon their thickness. It is noteworthy that the value of n for soybean flakes was found to be substantially the same for different lots of seed of varying moisture content flaked by different methods, and that the data of King et al.[44] obtained by trichloroethylene extraction indicated a value for n

exactly in line with the results with hexane, as well as a comparable value for K.

There is evidence[44] that large seed particles rolled to form flakes of a definite thickness can be extracted more rapidly than small particles, presumably because they undergo greater internal disruption in the rolling process.

3. Extraction Standards

Based chiefly upon experience with soybeans, it is generally considered that to be efficient, commercial solvent extraction must reduce the oil content of the dry solid residue to less than 1.0%, and preferably to about 0.5%.

It does not appear certain that this is a reasonable standard for oil seeds generally, or even that there is a clear advantage in extracting soybeans down to this latter very low oil level. There is undoubtedly some fallacy in the common belief that the efficiency of extraction is to be judged simply by the amount of oil remaining in the meal. As indicated above, the last portions of "oil" or petroleum ether soluble material in the meal are in considerable measure not oil at all, but phosphatides and other nonglyceride impurities. Bull and Hopper[45] have reported a phosphatide content of 18.62% in the last 1.1% of material extracted from a sample of soybean flakes with commercial hexane at 40°C. Similarly, Karnofsky[7] has reported that a similar fraction had a refining loss of 81.5%. It is difficult to believe that the addition of such material to good oil could fail to have a decidedly adverse effect on the refining loss. It appears entirely possible that such adverse effect might well serve to more than counterbalance the increased oil yield, and thus actually reduce the amount of material recoverable as refined oil. Thus far, little attention has been given to the efficiency of oil seed extraction in relation to the yield and quality of the refined oil; yet the latter is the true measure of efficiency.

4. Solvents for Oil Extraction

The solvents in most common use in the United States for oil and fat extraction are light paraffinic petroleum fractions, recovered from natural gas. The more popular products are cuts of fairly narrow boiling range, which are distinguished according to the chain length of their principal components. One manufacturer lists the following general A.S.T.M. boiling ranges for four types of naphtha: pentane type, 86–95°F.; hexane type, 146–157°F.; heptane type, 190–208°F.; octane type, 212–284°F.[47]

[47] A. E. MacGee, *Oil Mill Gazetteer*, August, 1947; *Cotton Gin and Oil Mill Press*, August 9, 1947.

There is also some demand for a mixed hexane-heptane product with a boiling range of about 158–208°F., although it is generally felt that a product of wide boiling range merely combines the volatility and tendency toward high solvent losses of the lower boiling fraction with the tendency of the higher boiling fraction to be difficult to remove from the extracted oil and solid residue.[48] The hexane-type naphtha is the one most widely used and the one generally preferred for oil seed extraction, although the heptane-type product is also considered suitable for use in most modern plants. The pentane type finds limited use in the extraction of heat-labile products such as pharmaceuticals; the higher boiling products are required for the extraction of castor oil, which is not freely miscible with hydrocarbons except at somewhat elevated temperatures.

In Europe, where cyclic hydrocarbons are more commonly available, the preferred extraction naphtha in the past has been a product consisting predominantly of cyclohexane, which has a boiling range of about 160–185°F.

A preliminary laboratory study of a number of pure hydrocarbons with respect to their all-around desirability as solvents for the extraction of cottonseed has been published by Ayers and Dooley,[49] who consider paraffinic hydrocarbons preferable to cyclic hydrocarbons, and find methylpentanes the best of the former group. A commercially available methylpentane-type naphtha is listed as having a typical boiling range of 139–145°F.

Although solvent losses in American plants employing hexanes for extraction are inclined to be higher than in European plants using a higher boiling product, they are not excessive, and in well-operated soybean extraction plants do not exceed about 2 gallons for each ton of seed processed. At this rate, charges for solvent loss are less than for labor, power, or steam.[38a]

The American-produced extraction naphthas are substantially free from nitrogen- or sulfur-containing compounds and unsaturated hydrocarbons, and leave a residue upon evaporation of less than 0.0016%. They are sufficiently stable to be re-used indefinitely, are cheap, and are available in practically unlimited quantities. The only serious disadvantage to their use is their extreme flammability. Rather elaborate precautions are required to avoid fire or explosion hazard in the plants in which they are used. The proper safety measures have been discussed in detail by Bonotto[50] and MacGee et al.[51]

[48] A. E. MacGee, *Oil & Soap*, *14*, 324–327 (1937).
[49] A. L. Ayers and J. J. Dooley, *J. Am. Oil Chem. Soc.*, *25*, 372–379 (1948).
[50] M. Bonotto, *Oil & Soap*, *14*, 30–33 (1937).
[51] A. E. MacGee, L. J. Weber, and C. H. Senter, *J. Am. Oil Chem. Soc.*, *25*, 279–295 (1948).

The history, composition, and characteristics of American extraction naphthas have been recently reviewed by MacGee.[47,52] Detailed analyses of a popular hexane product have been published by Griswold and co-workers[53] and by MacGee.[52]

Some use has been made of trichloroethylene in small oil seed extraction plants.[54,55] This solvent has the great advantage of being noninflammable, and appears to be satisfactory insofar as its stability and solvent characteristics are concerned, but it acts as a poison for hydrogenation catalysts unless its removal from the oil is very thorough; its high price appears to make it possibly uneconomic except in small plants where increased charges for solvent loss may be balanced against the capital expenditure required for the provision of safety equipment in plants employing hydrocarbon solvents. However, it has been claimed[55] that solvent losses may be as low as 0.5 gallon per ton of soybeans processed. Trichloroethylene boils at about 188°F.

At one time, carbon disulfide was widely used in Europe for the extraction of olive press cake, to recover the inedible product termed olive oil "foots" or "sulfur olive oil." However, it is on no account a desirable solvent; it has never been used in the United States, and in Europe its use is rapidly declining in favor of petroleum naphthas, which yield an edible extract. Acetone has been used to some extent for the recovery of oil from wet materials, such as fish livers, as has also ethyl ether.[40]

Interesting recent laboratory developments include oil seed extraction processes employing isopropyl alcohol[56-58] and ethyl alcohol[59] as solvents. The former, unlike petroleum naphthas, effectively extracts gossypol from cottonseed, and thus offers a possible means of detoxifying the residue from this seed without the necessity for severe heat treatment. However, the miscella must be purified of phosphatides, carbohydrates, and other nonglyceride extractives if it is to yield a crude oil of low refining loss and good refined oil color. Purification is readily accomplished by liquid–liquid extraction with commercial hexane.[58] When cooled moderately, alcohol miscellas separate into two layers consisting principally of oil

[52] A. E. MacGee, *J. Am. Oil Chem. Soc.*, *26*, 176–179 (1949).

[53] J. Griswold, C. F. Van Berg, and J. E. Kasch, *Ind. Eng. Chem.*, *35*, 854–857 (1943).

[54] I. J. Duncan, *J. Am. Oil Chem. Soc.*, *25*, 277–278 (1948).

[55] O. R. Sweeney and L. K. Arnold, *J. Am. Oil Chem. Soc.*, *26*, 697–700 (1949); O. R. Sweeney and L. K. Arnold (to Iowa State College Research Foundation), U. S. Pat. 2,497,700 (1950).

[56] W. D. Harris, F. F. Bishop, C. M. Lyman, and R. Helpert, *J. Am. Oil Chem. Soc.*, *24*, 370–375 (1947).

[57] W. W. Meinke, B. R. Holland, and W. D. Harris, *J. Am. Oil Chem. Soc.*, *26*, 532–534 (1949).

[58] W. D. Harris, J. W. Hayward, and R. A. Lamb, *J. Am. Oil Chem. Soc.*, *26*, 719–723 (1949). W. D. Harris and J. W. Hayward, *ibid.*, *27*, 273–275 (1950).

[59] A. C. Beckel, P. A. Belter, and A. K. Smith, *J. Am. Oil Chem. Soc.*, *25*, 10–11 (1948); U. S. Pat. (to Secretary of Agriculture) 2,445,931 (1948).

and of solvent; hence with such a solvent equipment and steam for the evaporation and recovery of solvent may be greatly reduced.

A recently issued patent[59a] of great interest claims the use of a hydrocarbon solvent mixed with a minor proportion of anhydrous methyl alcohol for the extraction of cottonseed. According to the specification of the patent, the methyl alcohol serves to convert gossypol in the seed substantially to a bright yellow, insoluble, and nontoxic material; thus the process avoids the necessity for detoxifying seed or meal by subjecting it to severe heat treatment, with accompanying injury to its nutritive value. Other alcohols, such as ethyl or isopropyl alcohol, are ineffective. According to Hutchins,[60] a mixed solvent process has for some time been actually in successful commercial operation.

On a pilot plant scale, soybean flakes have been extracted successfully with a mixture of trichloroethylene and ethyl alcohol.[60a]

5. TYPES OF EXTRACTORS

(a) Batch Extractors

Batteries of batch extractors are still in use in Europe for the recovery of oil from oil seeds or mechanical press residues. However, in modern plants batch equipment is used principally in the form of small units for the recovery of pharmaceutical oils or other expensive oils, for the extraction of spent bleaching earth, for the processing of meat scraps, cracklings, and garbage, or for other purposes where the tonnage of material handled does not justify the expense of installing continuous extractors. The largest single use of batch extractors in the United States at the present time is probably for the processing of castor pomace remaining from the cold-cage pressing of castor beans.

Batch extractors vary greatly in design. An extractor which is popular in the castor oil industry (Fig. 78) consists of a large horizontal drum (18 by 8.5 ft.) mounted on rollers by means of which the drum can be rotated on its longitudinal axis. Inside the drum is a horizontal, perforated, metal strainer covered with a filter mat of burlap, which extends the length of the drum and divides it into two compartments, one of which is much smaller than the other. The large compartment receives a charge of 10 to 12 tons of solid material through which solvent is percolated, to drain into the smaller compartment by gravity, from which it is continuously pumped during the drainage period. Four to six successive ex-

[59a] R. P. Hutchins and W. H. Williamson (to Procter & Gamble Co.). U. S. Pat. 2,484,831 (1949).

[60] R. P. Hutchins, Proceedings of a Six Day Short Course in Vegetable Oils, American Oil Chemists' Society, University of Illinois, 1948, pp. 70–76.

[60a] S. G. Measamer, O. R. Sweeney, and L. K. Arnold, Proc. Iowa Acad. Sci., 54, 189–197 (1947).

tractions suffice to reduce the oil content of castor pomace from about 15% to 1.5%. A common European extractor, somewhat similar, but of a stationary vertical design with internal mixing arms, has been described by Goss.[46]
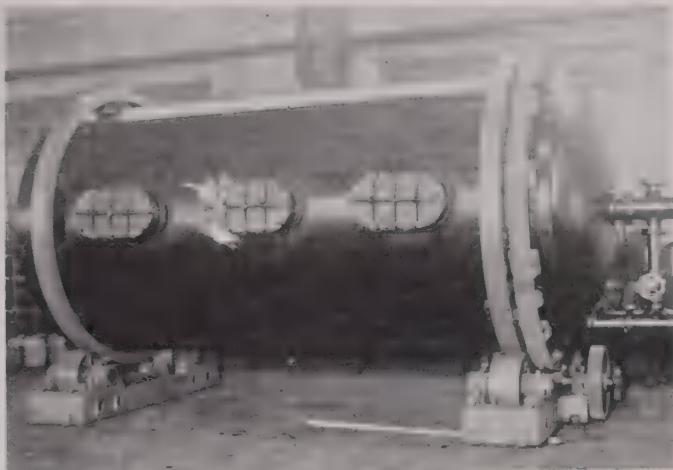
Fig. 78. Rotary extractor, for extraction of castor pomace, etc. (courtesy *The C. O. Bartlett & Snow Co.*).

The extractor commonly used for the extraction of garbage consists of a vertical cylindrical kettle, with a large ratio of diameter to depth, equipped with a vaportight cover, a steam jacket, and a vertical low-speed agitator. The most popular unit is about 4 feet, 6 inches in height, and 10 feet in diameter, and takes a charge of 3 to 5 tons of material. This extractor is suitable also for the extraction of other relatively wet materials, as the material may be dried and extracted in the same vessel.

Solvent systems are used to some extent for the extraction of fish liver oils, as well as fish oil. The equipment used for this purpose is described by Brocklesby.[2] A number of other types of batch extractors are described by Werth.[61] The extraction of miscellaneous oil-containing materials, as well as oil seeds, has been developed to a much higher degree in Europe than in the United States.

(b) Continuous Extractors[46,60,61,61a]

The oldest successful continuous oil seed extractor, and one that is still considered the best type by many, is the Bollman or Hansa-Mühle extractor,[62] otherwise known as the paternoster or basket type. This ex-

[61] A. van der Werth, in *Chemie und Technologie der Fette und Fettprodukte*. Vol. I, *Chemie und Gewinnung der Fette*. H. Schönfeld ed., Springer, Vienna, 1936, pp. 677–748.
[61a] G. Karnofsky, *J. Am. Oil Chem. Soc.*, 26, 570–574 (1949).
[62] H. Bollman, German Pats. 303,846 (1919) and 322,446 (1920); British Pat. 156,905 (1921). Hansa, Mühlenbau und Industrie, A.-G., German Pat. 670,283 (1939); British Pat. 507,465 (1939).

tractor was designed and first built in Germany; the American-built Blaw-
Knox and French extractors are very similar.
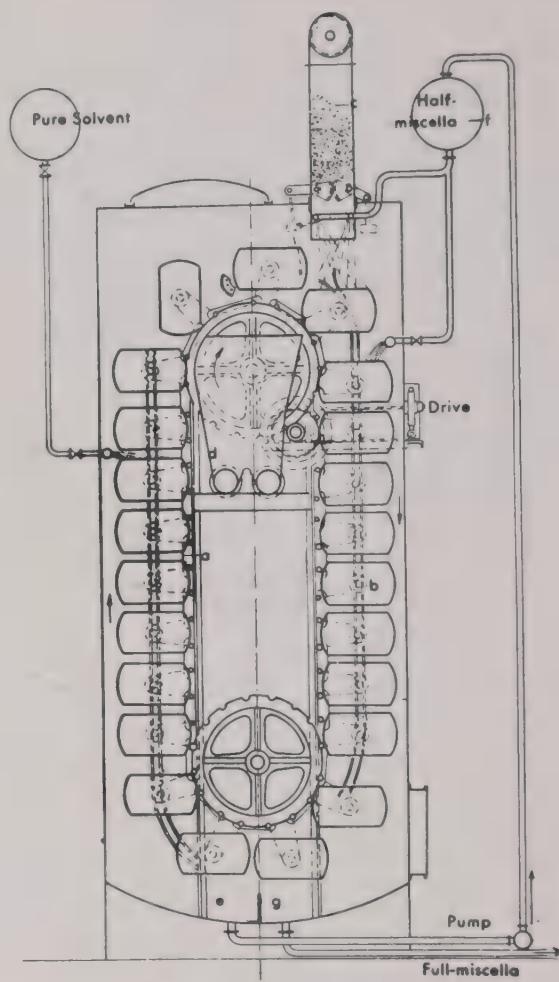
Fig. 79. Basket-type extractor.

The basket-type extractor (Figs. 79 and 80) has the appearance of an
enclosed bucket elevator. Unlike the various types of continuous extract-
ors to be described later, it does not immerse the oil seed flakes in the
solvent, but extracts by percolation of solvent through the seeds while
they are held in a series of baskets with perforated bottoms. To insure
uniform percolation and drainage, the width and depth of the baskets
are usually fixed, and the length is varied according to the capacity of
the extractor; common dimensions are 20 inches deep, 30 inches wide, and
40 to 85 inches long.[60] The baskets (usually 38 in number in the earlier
models) are supported on endless chains; within a gastight housing. The
flaked oilseeds are conveyed by a screw into a closed charging hopper at
the top of the housing, the completely filled conveyor tube serving as an

effective vapor seal against the solvent vapors inside the extractor. The baskets are continuously and very slowly raised and lowered, at the rate of about one revolution per hour. As each basket starts down the descending side of the apparatus, a charge of seed is automatically dropped into it, from the charging hopper. Extraction is effected by the percolation of
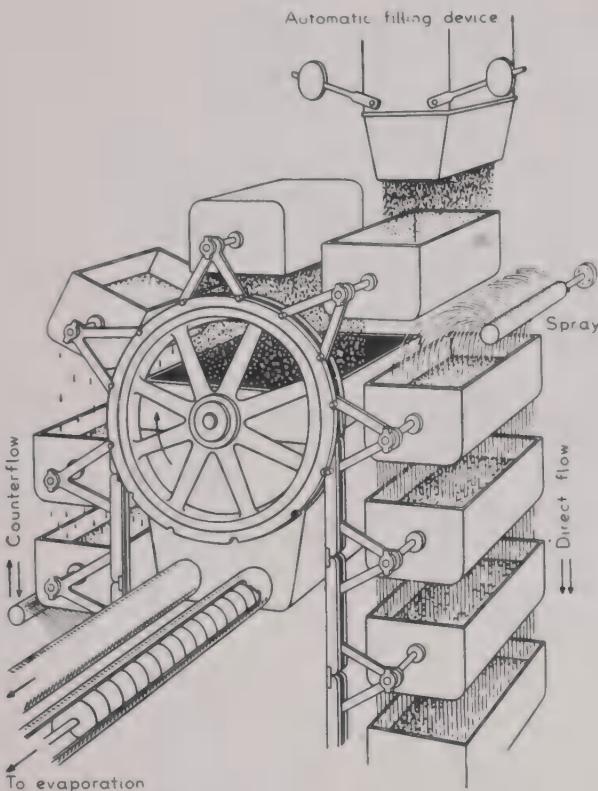
Fig. 80. Interior of basket-type extractor, showing schematically filling and dumping of baskets and flow of solvent.

solvent through the seed during their passage from the top to the bottom, and again to the top of the apparatus. As the baskets containing the spent and drained flakes ascend to the top of the housing, on the opposite side from the charging hopper, they are automatically inverted, and the contents are dumped into a discharge hopper, from which they are conveyed by means of screw conveyors to the meal driers.

Fresh solvent at the rate of approximately one pound of solvent per pound of seed is sprayed into a basket near the top of the ascending line of baskets, from which it percolates by gravity through the lower baskets, in countercurrent flow. The miscella from this side, termed the "half-miscella," is collected in a sump in the lower part of the housing. A pump continuously withdraws it from the sump and spray it into the topmost

basket of the descending line. From this basket it percolates downward through the lower baskets, similarly to the fresh solvent introduced on the other side of the system and is collected in a separate sump as "full-miscella." The full-miscella is freed from fine seed particles and solvent, to yield the finished oil, by means which will be described later.
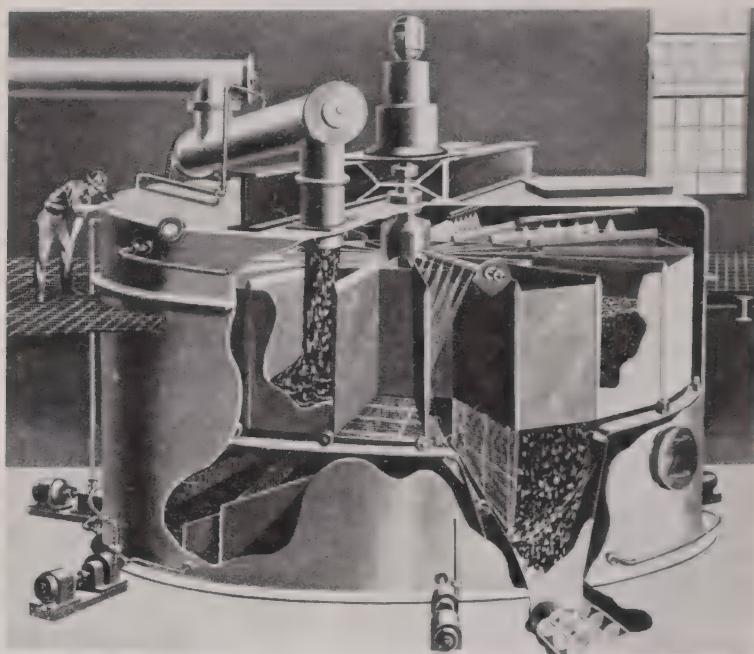
Fig. 81. Rotocell extractor (courtesy *Blaw-Knox Construction Co.*).

Detailed operating data on a modified 400-ton per day Hansa-Mühle plant processing soybeans have been published recently by Kenyon, Kruse, and Clark.[63]. Commercial hexane at a temperature of 136°F. is used as the solvent at the rate of 960 pounds[64] per 1000 pounds of flakes (9.5% moisture content), to reduce the oil content of the finished meal (containing 8.0% moisture) to 0.6–0.7% and produce a full miscella containing 25–28% oil. The extracted and drained flakes leaving the extractor retain about 35% of their own weight of entrained solvent.

Most of the basket-type extractors thus far built have been large, with capacities of the order of 200–400 tons of flakes per day, although one American plant is rated at but 75 tons per day.

The Blaw-Knox Rotocel extractor[61a,64a] is similar in principle to the

[63] R. L. Kenyon, N. F. Kruse, and S. P. Clark, *Ind. Eng. Chem.*, 40, 186–194 (1948).
[64] This corresponds to about 168 gallons at 60°F. or 178 gallons at 136°F.
[64a] K. McCubbin and G. J. Ritz, *Cotton Gin & Oil Mill Press*, 52, No. 6, 40–42 (1950); *Chem. Ana.* 354–316 (1950). G. Karnofsky, *Chem. Eng.*, 57, No. 8, 108–110 (1950).

basket extractors described above; however, the baskets are carried in a rotary motion in a single horizontal plane, and miscella percolating through the baskets and falling into compartments in the bottom of the extractor housing is picked up and recirculated countercurrent to the flakes by a series of pumps. The first commercial unit, placed in operation on soybeans in early 1950, employs 18 cells and six stages of extraction. It operates in a housing 12 feet in height and 22 feet in diameter, and has a capacity of 250 tons per day.[64a] It is said [61a] to have all the advantages of the conventional basket-type extractor without some of its disadvantages, being more compact and more flexible in operation.

The principal advantage of the basket-type extractor is that it yields a very clean miscella, with a minimum content of fines, from the circumstance that the flakes are not subjected to mechanical disturbance during the extraction period, and that the descending baskets form an effective series of filter beds for the half-miscella from the ascending baskets, where most of the fines production occurs. Its principal disadvantages are that it permits the possibility of channeling of solvent flow through the seeds, and that some oil seeds tend to pack in the baskets and become relatively impervious to percolation, with the result that the extraction rate becomes slow and the size of extractor required for a given capacity becomes unduly large. It should be noted, however, that materials which are difficult to process in the basket-type extractor likewise complicate the operation of extractors of other types.

Another early German extractor, the Hildebrandt,[65] consists essentially of two vertical tubes interconnected at the bottom by a third horizontal tube, with motor-driven screws to propel the flakes down one tube, across, and up the other tube countercurrent to the flow of solvent. Because of the working given the flakes by the screws, flake disintegration and fines production is relatively extensive; for this reason it is unsuitable for seeds such as cottonseed, although it has been reasonably successful in the processing of soybeans. A number of installations are in operation, in this country and abroad. Although the original Hildebrandt extractor is no longer manufactured, a modified design with screw propulsion of the flakes is to be found in the Ford extractor,[66] and the modern counterpart of the latter apparatus, the Detrex extractor. A variation in design consists of the substitution of a drag-link conveyor for the flake-propelling screws.[55] All of these latter extractors are designed for the use of a chlorinated solvent, and are intended primarily for the small-scale extraction of soybeans, e.g., at the rate of about 25 tons per day.

The Bonotto extractor[67] (Fig. 82) has a column divided into a number

[65] K. Hildebrandt, German Pats. 528,287 (1931) and 547,040 (19??); U. S. Pat. 1,961,420 (1934).

[66] H. Joyce, Oil & Soap, 12, 68–70 (1935).

[67] M. Bonotto (to American Soya Products Cor. .181 (1937); (to Extractol Process, Ltd.) 2,112,805 (1938); .48 (1939).
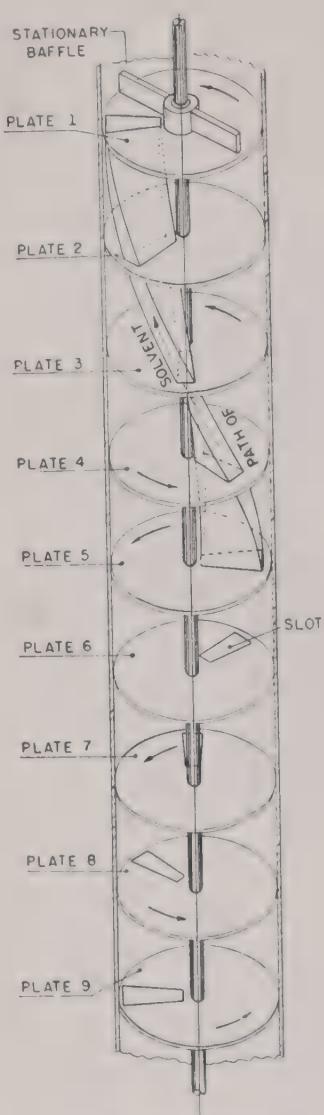
Fig. 82. Phantom view of Bonotto extractor column, showing revolving plate assembly with slots for downward movement of flakes and upward movement of solvent. Stationary baffle or scraper arm is shown in top section only (courtesy *Foster Wheeler Corp.*).

of sections by a revolving assembly of horizontal plates attached to a central shaft. The plates are provided with a series of staggered slots through which the flakes, introduced at the top of the column, proceed downward by gravity, countercurrent to a rising flow of solvent. Stationary scraper arms placed just above each plate provide gentle agitation of the flake mass to prevent packing or bridging, and assist in moving the flakes through the slots. The original Bonotto extractor employed a screw discharge with choke mechanism to compress the spent flakes and seal the bottom of the column against the escape of solvent. Discharge of the flakes through such a mechanism has the advantage of squeezing out most of the entrained solvent. With some seeds, however, it is not mechanically reliable; hence in extractors of the Bonotto type, operating on seeds other than soybeans, it has generally been replaced with an inclined side tube, up which the spent flakes are carried by a Redler or drag-link conveyor, through a set of squeezing rolls.

The latest Bonotto design[68] uses a Redler conveyor within a closed loop to feed the column, and filters the miscella from the column through the flakes in a portion of the loop before it is discharged. This assists in clarifying the miscella, and also extracts considerable oil from the flakes before they enter the extractor proper.

The Allis-Chalmers and Anderson extractors are modifications of the Bonotto apparatus; each employs stationary plates or partitions and moving scraper arms within the column, rather than moving plates and stationary baffles, and there are other structural differences, as well as differences in the auxiliaries The Anderson extractor for soybeans uses a

[68] M. Bonotto (es, Ltd.), U. S. Pat. 2,370,138 (1945).

choke or plug-forming flake discharge and has a built-in, mechanically operated device for settling fines out of the miscella[8a]; the Allis-Chalmers extractor uses an inclined side tube discharge for all oil seeds.

Extractors of the above type are generally built for a capacity of about 100 tons per day, hence they may be considered medium-sized units. Very large plants would presumably employ multiple extraction columns.
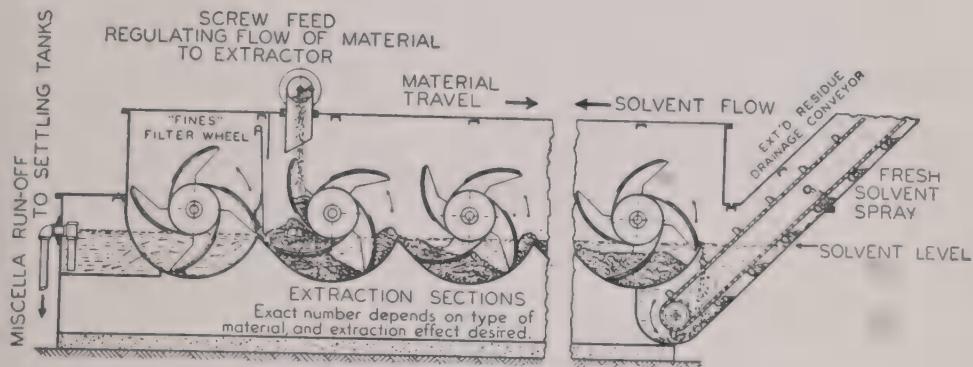
Fig. 83.   Kennedy extractor (courtesy *Vulcan Copper and Supply Co.*)

The Kennedy extractor[69] (Fig. 83) is built in the form of a long enclosed trough, which is divided into a number of sections, each of which has a rounded bottom. An impeller wheel carrying four curved and perforated blades revolves in each section, with the blade tips closely following the contour of the rounded bottom. Material introduced into the first section is transferred the length of the trough, from section to section, by the scooping action of the impeller blades, as the solvent flows through the bottom of each section, in a counter direction. As the material is lifted up the curved section wall above the liquid level, to fall into the succeeding section, it is compressed slightly between the impeller blade and the wall; this squeezes out some of the entrained solvent, and serves to decrease the carry-over of solvent from one section to another by the flakes. From the final section they are carried up an inclined tube and out of the extractor by a drag conveyor.

Many other continuous extractor designs have been patented, and a few have been used commercially, in Europe or South America. Of these, the Miag[70] and Fauth[71] extractors deserve particular mention. For more detailed descriptions of these, as well as the more common extractors mentioned previously, reference may be made to the publications of Goss,[46] Werth,[60] Alderks,[18] and Langhurst.[8a]

[69] A. B. Kennedy, U. S. Pat. 1,628,787 (1927). See also F. Lerm 2. Kennedy and J. Loshin, *Ind. Eng. Chem.*, 40, 1753–1758 (1948).
[70] Miag, Mühlenbau und Industrie A.-G., German P 570
[71] P. L. Fauth, German Pat. 356,304 (1919); Brit

A recently described plant for the commercial extraction of castor oil[72] departs from the conventional practice of forming flakes and striving to maintain the flake structure throughout the extraction process by grinding the seed and extracting the finely distintegrated material in three successive stages in which it is alternately mixed with the counterflowing solvent and separated by centrifugation in continuous Bird centrifugals. Heptane is used as the solvent at a temperature of 170°F. According to Pascal,[73] miscellas containing oil in the range of 8–22% can advantageously be separated, by cooling, into an oil-rich and an oil-poor phase, with the latter being re-used as a solvent without distillation. Commercial heptane and castor oil are miscible in all proportions above about 31°C., which is well below the preferred extraction temperature of 50°C., but good separation occurs upon cooling a 20% miscella, *e.g.*, to 20°C.

6. Recovery of Solvent

(a) *Recovery from Miscella*

Miscella from the solvent extractor must be freed of finely divided solid material before it is processed for oil recovery. It is possible to clarify the oil after the solvent is removed,[38a] but the presence of fines complicates the operation of solvent stills, and this method also leads to excessive losses of oil entrained in the fines, unless the latter are well washed. It is generally not considered advantageous to recycle a large amount of separated fines through the extraction equipment.

The amount of fines to be handled varies greatly with different oil seeds and different types of extractors. Basket-type or percolation extractors processing soybeans produce very little fines, and the miscella is simply filtered, usually through leaf-type filters, which must be cleaned only occasionally. In processing non-pre-pressed seed such as cottonseed through extractors of the immersion type, a considerable proportion of fines is obtained, which must be handled with special equipment and washed to reduce the oil content if a high over-all extraction efficiency is to be maintained. Here, the tendency is to rely upon continuous centrifuges of the Bird type to remove most of the solid material, and filtration to provide the final clarification. None of the clarification systems thus far introduced appears to be altogether satisfactory where large amounts of fines are to be handled; current problems in the extraction of high-oil content seeds are largely a matter of fines prevention or efficient fines handling rather than a matter of difficulty in reducing the oil content of the seed.

[72] See *Ch____na___ , ___ 54, 926–929 (1949); also M. W. Pascal (to Sherwin-Williams Co.), U. S. ____ , ____ con__ (1__9).
[73] M. W. P____ ___ , ___ ___ __lliams Co.), U. S. Pat. 2,467,403 (1949).

Recently it has been reported[73a] that 0.15–0.30% of fines in the miscella have been successfully removed on a commercial scale by injecting 1–4% water plus a wetting agent to effect hydration of the fines, and separating the hydrated material plus a small quantity of emulsion in centrifuges of the fixed-nozzle or automatic valve type.

The original Hansa-Mühle plant effected recovery of solvent from the oil in three stages; the miscella containing 20–25% oil was passed in series through two steam-heated pot stills to reduce the solvent content to about 50%, then through a falling film evaporator, where it was reduced to 5–10%, and finally through one or two steam-stripping columns of the packed type, where the last portions were removed. In the American-built plants the pot stills have been replaced by miscella preheaters and rising film evaporators with entrainment separators. In some cases the falling film evaporator has been retained or replaced with a small rising film evaporator operated with sparging steam; in others, miscella from the first large rising film evaporator goes direct to the stripping column. Usually the stripping column is maintained under reduced pressure with a steam ejector. The American equipment is more compact, and with it the miscella is kept hot for a shorter period. In the extraction of cottonseed oil, in particular, prolonged heating of the oil or miscella will "set" the color and produce a permanently dark oil.[74] However, no difficulty in this respect has been encountered in plants using the rapid evaporation equipment described above.

Many soybean processors operate degumming and lecithin recovery plants in connection with solvent extraction plants. In the past, some plants have purposely allowed some condensation of stripping steam to occur in the stripping column, to hydrate the phosphatides and deliver an oil ready for passage through the degumming centrifuges.

Systems comprising a fatty oil and hexane or other hydrocarbon solvent exhibit a considerable negative deviation from ideality, i.e., the vapor pressure of the solvent is lower than calculated from its molar concentration in the miscella and the vapor pressure of the pure solvent, upon the basis of Raoult's law. Below a solvent concentration of about 10% by weight, the boiling point becomes so high that steam stripping is essential in the final stages of solvent recovery.

Boiling point and vapor pressure data on mixtures of commercial hexane with cottonseed and peanut oils have been published by Pollard et al.[75] Values for the boiling points of cottonseed–hexane mixtures at different pressures, as derived from their smoothed data, are shown in

[73a] J. M. Crockin, *Chem. Eng.*, No. 11, 160–162 (1950).
[74] For information on the darkening of cottonseed oil in relation to ti̶e̶ and temperature of heating the miscella, see H. L. E. Vix, E. F. Pollard, 2. ̶ ̶daro, and E. A. Gastrock, *Ind. Eng. Chem.*, *38*, 635–642 (1946).
[75] E. F. Pollard, H. L. E. Vix, and E. A. Gastrock ̶ ̶ ̶7, 1022–1026 (1945).

Table 106. These may well be analyzed in some detail, inasmuch as they constitute virtually the only published data of their kind that are both

TABLE 106

BOILING POINTS (°F.) OF MIXTURES OF COTTONSEED OIL AND COMMERCIAL HEXANE[a]

Oil in mixture, wt. %	Pressure, mm.				
	760	610	460	310	160
0	152	140	124	105	80
50	158	145	130	111	82
60	162	150	133	114	85
70	171	157	140	120	91
80	186	172	154	132	102
85	201	186	167	144	113
90	231	210	189	163	129
92	248	226	203	177	142
94	273	250	224	192	156
95	289	268	238	203	165
96	—	—	254	215	177
97	—	—	271	230	190
98	—	—	—	248	207
99	—	—	—	272	229

[a] From the data of E. F. Pollard, H. L. E. Vix, and E. A. Gastrock, *Ind. Eng. Chem.*, **37**, 1022–1026 (1945).
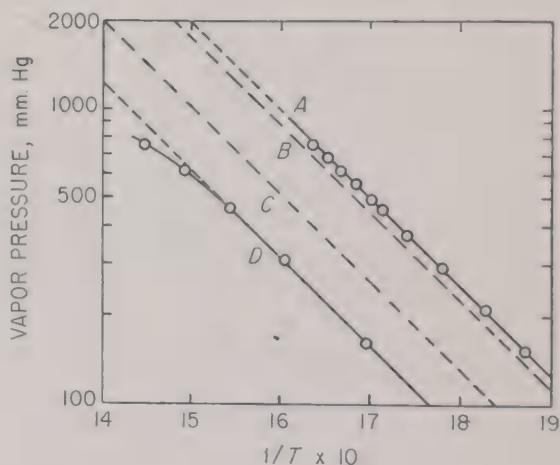
Fig. 84. Vapor pressure curves: (*A*) commercial hexane; (*B*) pure hexane; (*C*) 10% commercial hexane in mixture with cottonseed oil, ideal curve; (*D*) same mixture, actual curve, according to data of Pollard *et al.*[75]

accurate and comprehensive. In Figure 84 are plotted vapor pressure curves for pure hexane, for commercial hexane, as experimentally determined, and for a 10% commercial hexane miscella, both as calculated for an ideal mixture, and as actually determined; the plots are on the conventional basis of vapor pressure *vs.* reciprocal of the absolute

temperature, to give straight lines. It will be seen that below a temperature of about 200°F. (corresponding to a value of $1/T$ of 15.16), the actual vapor pressure curve of the miscella is a straight line, with a slope equal to that of the vapor pressure curve of the pure solvent or of the ideal curve, but considerably below the latter. Assuming an average molecular weight for the oil of 865 and for the solvent of 86, the mol per cent of solvent in a mixture containing 10% solvent by weight is 52.8, hence
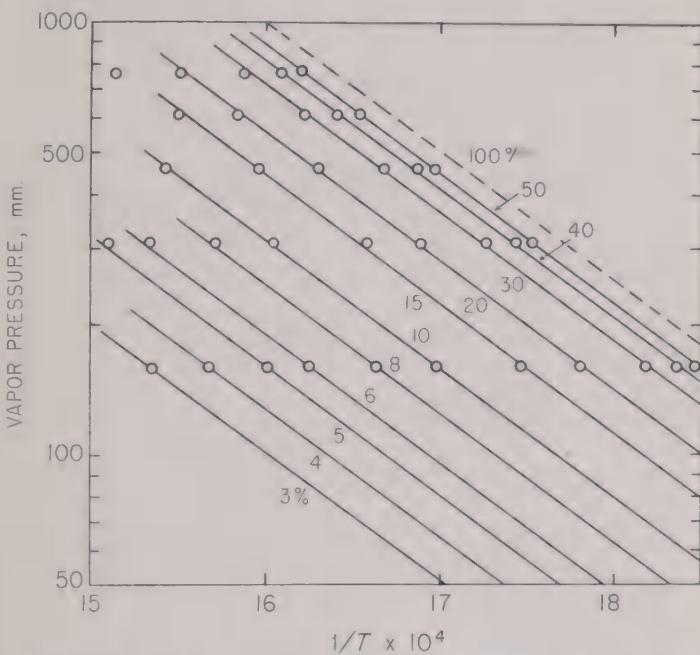
Fig. 85. Vapor pressure curves of commercial hexane in different concentrations by weight in mixtures with cottonseed oil. From data of Pollard et al.[75]

the ideal vapor pressure is at any temperature 52.8% of that of the solvent alone. The *activity coefficient* or ratio of actual vapor pressure to ideal vapor pressure over the linear portion of the actual vapor pressure curve may be determined from the figure; at a value of $1/T$ of 16, for example, the actual vapor pressure is 310 mm., whereas the ideal vapor pressure is 520 mm.; hence the activity coefficient is $310/520 = 0.60$.

Similar plots and calculations may be made for miscellas of other concentrations where experimental values have been determined at temperatures below 200°F.; the graphical data are shown in Figure 85, and in Figure 86 activity coefficients are shown in terms of the composition of the miscella. Although data at very low solvent conce˜˙ ˙ions are not available, it appears from Figure 86 that at such ˖ 2,˙ ˙ions the vapor pressure of the solvent can probably b˖ ˙ ˙ ˙ ˙ ˙ ˙bout 40%

of the vapor pressure of the pure solvent, times the mol fraction of solvent in the miscella. For leaner miscellas, where boiling occurs at reasonable temperatures, and steam stripping is not required, the data in Table 106
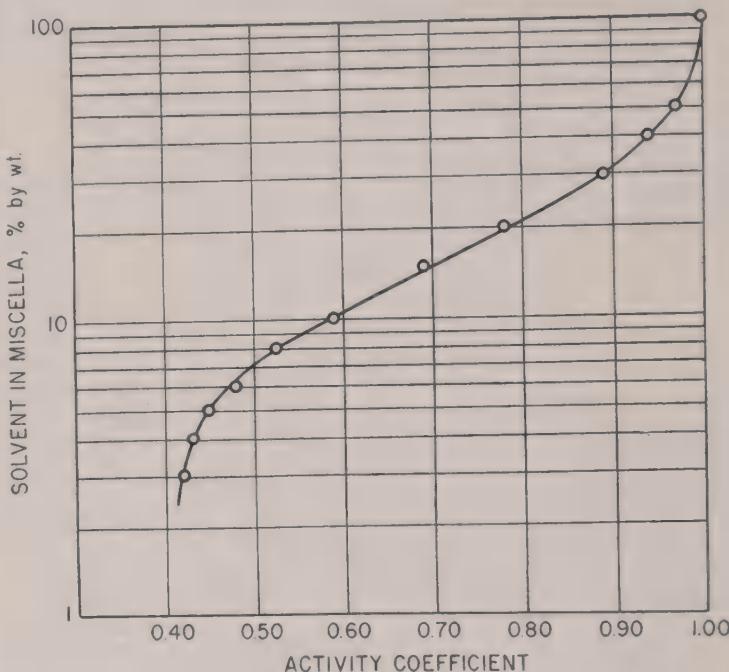
Fig. 86.   Activity coefficients of commercial hexane in admixture with cottonseed oil. From data of Pollard et al.[75]

will be directly applicable. It should be mentioned that the values from which the table was derived were determined in a laboratory apparatus with vigorous stirring to prevent superheating of the solvent. In ordinary apparatus considerable superheating may be expected.

Very recently, Smith and Wechter[75a] have published data on the vapor pressures of mixtures of soybean oil with Eastman practical grade hexane in the range of 75–120°C. and 2–36 mole per cent or 0.20–5.25 weight per cent solvent. See Figure 87 on page 605. Calculated activity coefficients range generally between 0.50 and 0.60.

In making practical stripping calculations it is, of course, to be recognized that the last portions of solvent may consist in part of heavy ends of lower volatility than the original solvent.

(b) Recovery from Extracted Flakes

The standard equipment for desolventizing of the extracted flakes, originally of German design, consists of a series of horizontal steam-

[75a] A. S. con's and Wechter, J. Am. Oil Chem. Soc., 27, 381–383 (1950).

jacketed tubes through which the flakes are propelled by means of screws. For the final removal of the last traces of solvent or "deodorization" of the flakes, a similar, but larger tube is provided through which the flakes are passed countercurrent to a current of stripping steam. The
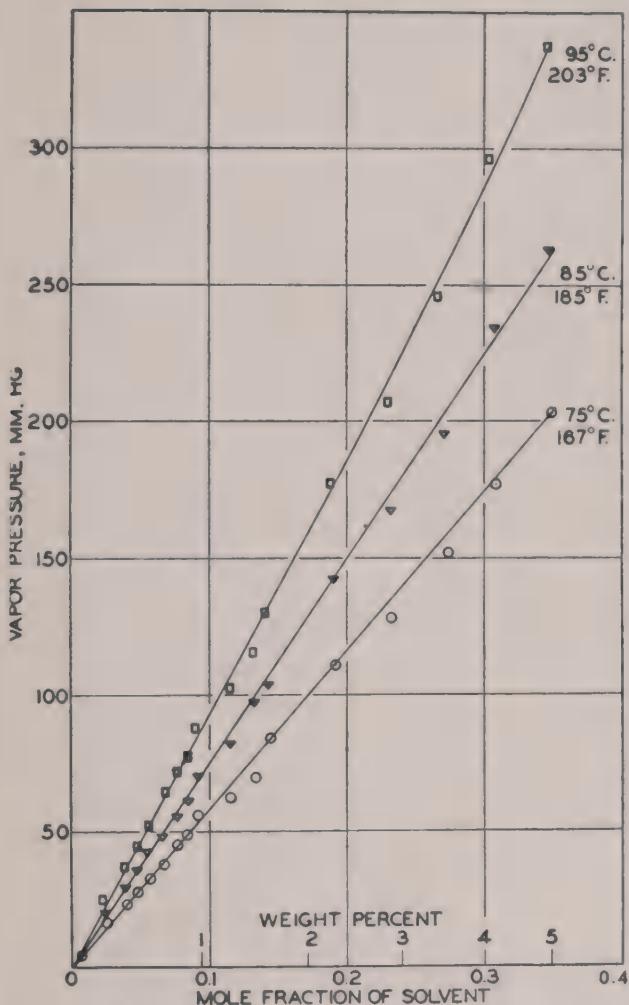
Fig. 87. Vapor pressure curves for low concentrations of hexane in soybean oil.[75a]

American Blaw-Knox system employs a much more compact desolventizer through which superheated solvent vapors are passed simultaneously to heat the flakes and sweep out the vaporized solvent. The Bonotto system also includes a compact desolventizer of novel design.

When hydrocarbon solvents are used, the separation of condensed solvent and condensed stripping steam from the "deodorizer" and from the miscella stripping column is facilitated by the comparative immiscibility of the solvent and water; a continuous decanter or a 2, k is used to separate the solvent, which is re-used with   ent.

The extractor proper, all solvent and miscella tanks, and the various solvent condensers are all vented to a vent condenser or condensers which are protected by special means from loss of solvents. In some plants the vent condensers are refrigerated; in others they communicate with the atmosphere through charcoal-filled adsorbers which are periodically steamed for the recovery of solvent or through a packed column down which a small side stream of oil is diverted as an adsorbing agent. As indicated previously, solvent losses in the more efficient plants operating with a hexane-type solvent do not exceed two gallons of solvent (about 11.5 pounds) for each short ton of flakes extracted.

Vapors from the "deodorizer" and air from a final meal cooler may carry considerable dust, lint, etc., particularly if the extracted material is inclined to powder. Scrubbers, cyclone separators, etc., of various designs are used to collect dust and avoid fouling of the condensers and other portions of the solvent recovery system, as well as the formation of emulsions in the solvent–steam condensate separator.

7. AUXILIARY EQUIPMENT

Auxiliary equipment for pretreatment of the seed before they enter the extractor, and for treatment of the desolventized and deodorized flakes after they leave the extraction system, is shown for a typical soybean plant in Figure 88. The flake toaster shown in the figure is a stack cooker similar to that depicted in Figure 65 (page 562). However, many plants employ a more compact apparatus in which toasting is conducted under steam pressure.

E. Recovery of Oil from Fruit Pulps

The only fruit pulp oils of commercial importance are olive oil and palm oil. These oils must be recovered by techniques somewhat different from those employed for the treatment of either fatty animal tissues or oil seeds. The extraction of these oils will therefore be considered apart from the different processes which have been discussed previously.

1. EXTRACTION OF OLIVE OIL

The extraction of olive oil is in general carried out by less efficient and modern methods than most other vegetable oils, since the industry is highly decentralized and is distributed in many small establishments throughout the growing countries.

Notwithstanding the fact that olives are seldom transported long distances f... ...ducing groves to the extraction plants, they are often subjected... ...con... ...use prior to being processed. The rather gen-
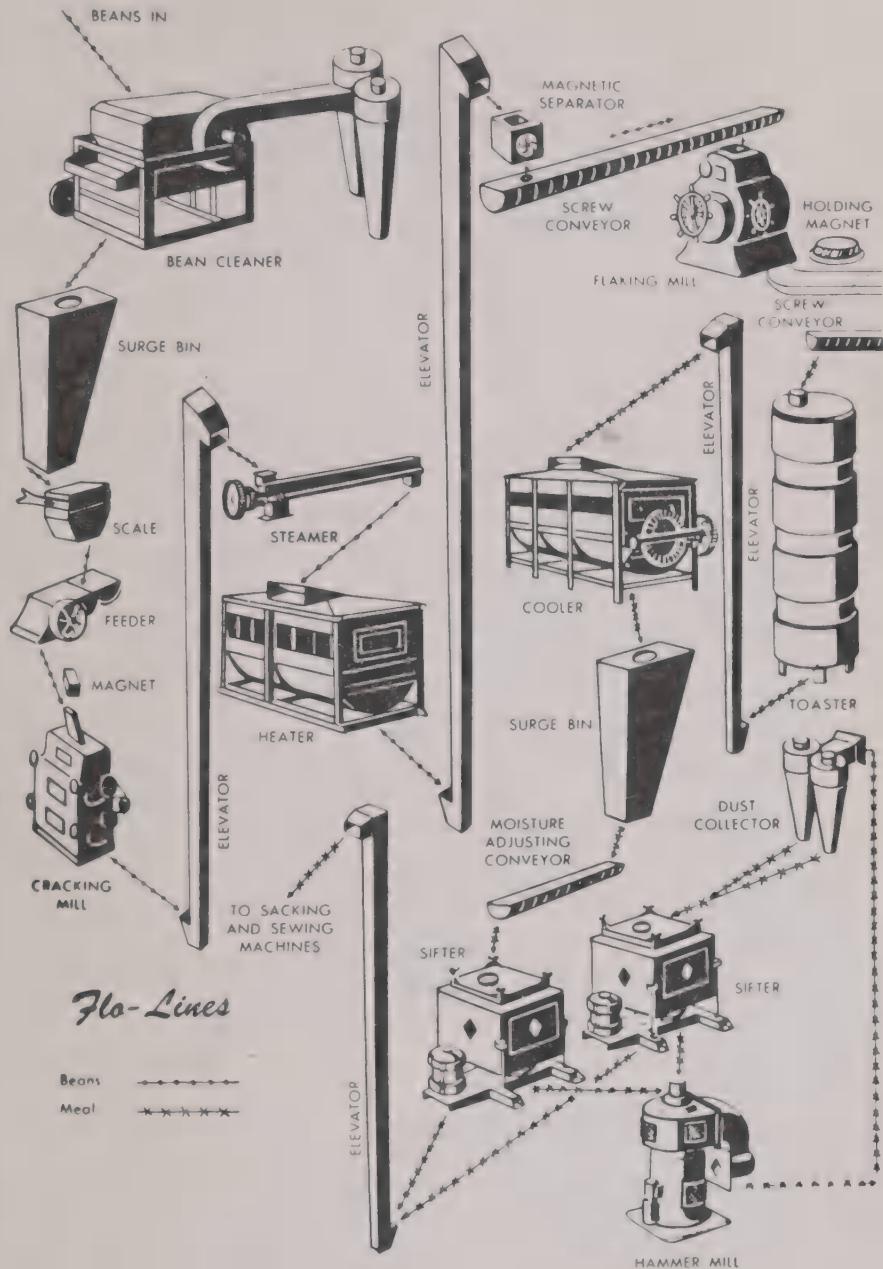
Fig. 88. Diagram of auxiliary equipment for soybean extraction plant, showing cleaner, heater, flaking mill, etc. for delivering flakes to extractor; and toaster, cooler, sifters, etc., for handling desolventized flakes returned from meal dryers. (Courtesy *Allis-Chalmers Manufacturing Co.*).

eral practice of bruising the fruit during harvesting, and ʰᵉⁿ storing it for protracted periods, accounts for the fact tʰᵃᵗ ... ²; ... ly has a rather high content of free fatty acids.

The equipment used for processing olives for oil varies greatly from one country to another, and even from mill to mill within the same country. Perhaps the most common method of preparing the pulp for expression comprises putting the fruit through mills of the edge-runner type, without cracking the fruit pits. The macerated pulp is then transferred to woven baskets or "scourtins," and the oil and water are expressed in a hydraulic press. The presses used for this purpose generally develop considerably less pressure than those used for the expression of oil seeds, since the fluid nature of the pulp mass precludes the application of very high pressures.

Pressing is carried out in two or more stages, with the first pressing yielding the highest grade, so-called "virgin" olive oil, and each subsequent pressing yielding a lower grade. Prior to the last pressing the cake is sometimes broken up and moistened with water, and in some cases it is subjected to a more thorough milling, with cracking of the olive pits. In all cases, heat treatment of the pulp or cake is avoided.

In the United States, hydraulic box presses are generally used for the recovery of olive oil, although there is also said to be some use of screw presses. It is said to be possible to press olive pomace mechanically to a residual oil content of 8%, although much of that produced in California runs as high as 12–13% oil.[76] The press cake or pomace is extracted with a hydrocarbon solvent, usually of the hexane type, and the extracted oil is refined, bleached, and deodorized, after which it is blended with other oil in the preparation of the grade of oil termed "pure olive oil." A similar method of processing is now also becoming common in the olive-producing sections of the Mediterranean region.

The expressed olive oil may be centrifuged to remove water and solid pulp particles, but more often it is clarified by settling and filtration. Water is not generally added to wash the oil or assist in the separation, since treatment with water is considered detrimental to the quality of the oil.

2. Extraction of Palm Oil

At one time, most of the palm oil on the market was extracted by African natives, by exceedingly primitive methods. In recent years, however, the production of oil from wild growing trees has been much exceeded by that from the plantations of the Netherlands East Indies, Malaya, and the Belgian Congo. The plantation oil has generally been extracted by modern methods, and is much superior in quality to the older African oil. Good plantation oil consistently runs lower than 5% in free fatty acids, whereas African native produced oil was not uncommonly as high as 15, 25 or ev̵̲ d̲b̲l̲e̲ ̲ ̲ free fatty acid content.

[76] R ̶ ̶ ̶ ̶ ̶ ̶ ̶ ̶ ̶ ̶ ̶ Soc., *24*, 315–316 (1947).

The sequence of operations in a well-operated palm oil extraction plant, as outlined by Bunting, Georgi, and Milsum,[77] is as follows: The ripened fruit bunches are first sterilized, upon receipt at the extraction plant, to inactivate lipolytic enzymes and loosen the fruits from the bunch sufficiently to permit threshing. Sterilization is conducted in large autoclaves, under an injected steam pressure of not more than 30 pounds, for about one hour. Sterilization requires approximately 350 to 400 pounds of steam per (long) ton of bunches. Normally, the sterilized bunches lose approximately 10% of the weight of the fruit as water. If the oil is to be subsequently extracted by means of centrifuges, excessive drying of the fruit is avoided. If the oil is to be expressed in hydraulic presses, however, a relatively dry fruit is desirable, and the normal sterilization period may be followed by one-half hour of vacuum treatment.

The sterilized bunches are run through strippers or threshers, to separate the fruit from stems and stalks, after which the separated fruit is treated in digesters. Digestion is different for press and hydraulic methods of extraction. If the material is to be pressed, digestion is carried out in an open, stirred, steam-jacketed kettle, with further dehydration occurring during the operation. If it is to be centrifuged, the digester is closed, and digestion is carried out under a few pounds of steam pressure. The contents of the digestor are discharged either to the presses or centrifuges, according to the system used. In either case, there is no separation of pulp and kernels prior to expression of the oil.

The presses used for palm fruits are of a special steam-heated cage design. The centrifuges used are of the basket type, and are totally enclosed and provided with a nozzle for the injection of steam during the extraction operation. They are ordinarily run 2–3 minutes without steam, then about 6 minutes with steam, then 2 minutes without steam.

The centrifugal and hydraulic press systems are equally efficient insofar as oil recovery is concerned; each recovers 85–90% of the oil in the pulp. In the case of centrifuged extraction, a residue is produced containing about 8.5% oil, 50% moisture, and 41.5% solid material. The cost of the plant is approximately the same for the two systems, and charges for labor and power are not significantly different. The press system expresses more oil, but the oil contains more solid material, and there are greater losses of oil in subsequent purification.

The extracted oil is purified by being heated in tanks with open steam and then either settled or centrifuged. Hydraulically pressed oil must have 40% of water added prior to purification, whereas centrifuged oil requires no such addition. A 250-gallon charge of the oil-water-pulp mix-

[77] B. Bunting, C. D. V. Georgi, and J. N. Milsum, *The Oil Palm . . . . . . laya*, Dept. Agr., Straits Settlements and Federated Malay States, Ku?'a 2,: 34.

ture yields 160 gallons of oil, 20 gallons of sludge, and 70 gallons of water by centrifugation. The oil content of the water is 0.05–0.10 pound per gallon.

It is possible, by means of a secondary pressing of the pulp residue, to recover approximately 50 % of the remaining oil, but such treatment is not economically feasible under all conditions of the palm oil market.

REFINING AND BLEACHING

The crude fats and oils produced by rendering, expression, or solvent extraction, contain variable amounts of nonglyceride impurities. In the case of high-grade animal fats and certain vegetable oils, such as coconut and palm kernel oils, these impurities consist principally of free fatty acids. There are significant amounts of other substances, however, in most vegetable oils, as well as in animal fats which have been rendered from low-grade materials. Thus, for example, Jamieson and Baughman[1] reported the following in crude cottonseed oil: raffinose, pentosans, resins, proteoses, peptones, phospholipins (phosphatides), phytosterols, phytosteroline, inosite phosphates, xanthophyll, chlorophyll, mucilaginous substances, and free fatty acids.

Not all of the impurities of crude oils are undesirable. The sterols are colorless and heat-stable, and for all practical purposes, inert; hence they pass unnoticed unless present in unusually large amounts. Tocopherols perform the important function of protecting the oil from oxidation. For this reason they may be classed as highly desirable constituents of most oil and fat products. However, most of the other impurities are objectionable, since they render the oil dark colored, cause it to foam or smoke, or are precipitated when the oil is heated in subsequent processing operations. The object of refining and bleaching is to remove the objectionable impurities in the oil with the least possible damage to either the glycerides, or the tocopherols or other desirable impurities, and with the least possible loss of oil.

As used here, the term "refining" refers to any purifying treatment designed to remove free fatty acids, phosphatides or mucilaginous material, or other gross impurities in the oil; it excludes "bleaching" and also "deodorization." The term "bleaching" is reserved for treatment designed solely to reduce the color of the oil. Very little material is removed from the oil by bleaching, and bleaching treatment is commonly applied to oils after purification has been largely accomplished by refining. "Deodorization" is the term used in reference to treatment which has as its primary object the removal of traces of constituents which give rise to flavors and odors, and which usually follows refining and bleaching. Re-

[1] G. S. Jamieson and W. F. Baughman, *J. Oil &* ⟨illegible⟩ 226).

fining and bleaching are closely related processes which will be treated together in this chapter; deodorization is accomplished by the use of entirely different techniques that will be covered in a separate chapter.

In Europe the most common method of refining—which involves the use of alkalies to react with free fatty acids in the oil—is ordinarily referred to as "neutralization."

A. General Considerations

1. REFINING AND BLEACHING METHODS

By far the most important and generally practiced method of refining is by treatment of the oil with an alkali. Alkali refining effects an almost complete removal of free fatty acids, which are converted into oil-insoluble soaps. Other acidic substances likewise combine with the alkali, and there is some removal of impurities from the oil by adsorption on the soap formed in the operation. Also all substances are removed which become insoluble upon hydration.

The alkali most commonly employed for refining oils is caustic soda, which is much more effective in its decolorizing action than weaker alkalies. Caustic soda has the disadvantage, however, of saponifying a small proportion of neutral oil, in addition to the free fatty acids. There is some use, therefore, of other alkalies, such as soda ash or sodium bicarbonate. Organic bases, such as the ethanolamines, have also been proposed as refining agents, because of their selective action toward the free acids in the oil.

Certain oil impurities, such as phosphatides, proteins or protein fragments, and gummy or mucilaginous substances, are soluble in the oil only in an anhydrous form, and can be precipitated and removed if they are simply hydrated. Hydration is accomplished by steaming the oil or mixing it with water or a weak aqueous solution. It may also occur when the oil is stored with access to the atmosphere; hence some vegetable oils tend to become purified naturally in storage, with precipitation and settling of so-called "foots."

Since free fatty acids are much more volatile than glycerides, it is possible to remove them from an oil by steam distillation at a high temperature under reduced pressure. So-called "steam refining" is similar to ordinary steam deodorization; with some fats it is possible to combine the two in one operation.

Recently, liquid-liquid extraction has come into prominence as a refining method, particularly for low-grade fats containing pigments that are diff ... ove by other methods. Extraction of the fat with a suita... con... arates most of the pigments and other non-

fatty impurities, but if properly applied may also effectively deacidify the oil (free fatty acid contents as low as 0.02–0.06% have been reported).

Oils, particularly those intended for use in paints, are sometimes "acid refined" by treatment with strong sulfuric acid. Acid refining does not reduce the free fatty acid content, but it chars and precipitates phosphatides and similar impurities.

The standard method of bleaching is by adsorption or treatment of the oil with bleaching earth or carbon. The various chemical bleaching methods applied to inedible fats all depend upon oxidation of the pigments to colorless or lightly colored materials. Most of the refining methods enumerated above accomplish considerable reduction of the color of the oil. The carotenoid pigments are not altogether stable to heat and are converted to colorless compounds by reduction, hence there are bleaching effects incidental to the operations of hydrogenation and deodorization.

2. Effect of Refining and Other Processing Treatment on Specific · Impurities

Alkali refining of an oil with caustic soda readily reduces the free fatty acid content to 0.01–0.03%. With a weaker alkali such as sodium carbonate, however, it is difficult to get the free fatty acids below about 0.10%. Steam refining with suitable equipment will also reduce the free acids to 0.01–0.03%. Degumming of a crude oil (with water) will often cause a substantial reduction in its titratable acidity, but not in its actual content of free fatty acids. Bleaching with earths or carbon has little effect on the acidity of oils, except in the case of certain acid-activated earths; these may increase the acidity appreciably, e.g., 0.05–0.10%, particularly if the oil is soapy or if the contact time is prolonged and the oil is not well dried. Free fatty acids can be removed from oils by chromatographic adsorption on alumina or silica gels, but a high ratio of absorbent to acids is required (10–30 to 1), and the process is uneconomic.[1a]

Alkali refining removes phosphatides from oils quite completely—in fact, it has been stated[2] that the phosphorus content of a refined oil is an acceptable criterion of the over-all efficiency of refining, and that it should not exceed about 0.5 part per million (0.00005%). This corresponds to about 0.0015% phosphatides. The phosphorus content of degummed soybean oils is of the order of 0.001–0.005%; that of non-degummed extracted oils is often as high as 0.10%.

Alkali refining, and to a lesser extent, degumming, also brings about the

[1a] M. Loury, Bull. mat. grasses inst. colonial Mar᷍
[2] M Mattikow, J. Am. Oil Chem. Soc., 25, 200-

removal of a certain amount of nonphosphatide oil-soluble material, including carbohydrates and protein fragments, although information as to specific compounds is not available. McGuire and coworkers[3] found in laboratory experiments that a crude soybean oil containing 0.019% nitrogen was reduced to 0.00044% nitrogen by one water washing, and to 0.00024% and 0.00019% by a second and third water washing. Alkali refining and bleaching of the original crude and of the once-, twice-, and three-times water-washed oil yielded products with 0.0009, 0.00016, 0.00012, and 0.00009% nitrogen, respectively. Deodorization further reduced the nitrogen to ca. 0.00005% in all cases. Samples of commercial soybean, cottonseed, and corn salad oils were found to contain 0.00002, 0.00003, and 0.00014% nitrogen, respectively. Much of the nitrogen was, of course, in each case in the form of phosphatides. The ratio by weight of phosphorus to nitrogen in soybean oil phosphatides is about 2.7 to 1[3a]; ratios of 2.4–3.0 to 1 have been reported for purified cottonseed oil phosphatides.[3b]

Acid refining likewise removes phosphatides and related substances, or "break material," quite completely. At the high temperatures employed in steam refining the oil will break and insoluble material will be precipitated if phosphatides are present in any considerable amount; if a moderate amount of phosphatides is present, no visible separation of solid material will occur, but the oil will become dark colored, presumably from the decomposition of associated carbohydrates. If the phosphatide content is less than about 0.02%, no such effect is observed.[4]

Treatment of an oil with bleaching earth is quite effective in removing phosphatides and the various mucilaginous materials referred to as "gums," "slimes," etc. A crude fish oil, for example, which can be hydrogenated only with great difficulty because of the poisoning effect of such materials on the catalyst, can be readily hydrogenated after a heavy treatment with an acid-activated earth. Nickel hydrogenation catalysts are even better adsorbents than are bleaching earths for many impurities, and are often effective after they have been used sufficiently to have become largely inactive for hydrogenation. Hence treatment of an oil with a "spent" catalyst is often a useful purification method.[4a]

Gossypol and related pigments of cottonseed oil readily combine with caustic soda, and thus are removed more or less completely by alkali refining. Oils which are presumably colored only by carotenoid pigments

[3] T. A. McGuire, F. R. Earle, and H. J. Dutton, J. Am. Oil Chem. Soc., 24, 359–361 (1947).

[3a] C. R. Scholfield, H. J. Dutton, F. W. Tanner, Jr., and J. C. Cowan, J. Am. Oil Chem. Soc., 25, 368–372 (1948).

[3b] B. H. ....rman (to Refining, Inc.), U. S. Pat. 2,201,061 (1940). H. S. Olcott. Science .... (1944).

[4] S. ..... con.... ..ley and R. O. Feuge, Oil & Soap, 21, 286–288 (1944).
..... U. S. Pat. 2,413,009 (1946).

are also lightened by alkali refining, although it is probable that the pigments are physically adsorbed on the soap formed by the alkali, rather than chemically combined. However, the adsorptive capacity of the soap is limited; palm oil, which is very strongly colored by carotene, is apparently little affected in color by alkalies. Caustic soda is said to have no effect on the color of tung oil.[5]

Acid refining ordinarily reduces the red and yellow color of vegetable oils to a greater extent than does alkali refining,[5] particularly if the oil is of relatively poor quality. Most vegetable oils lose considerable red and yellow color from heat treatment alone, although, as will be seen later, such oils may exhibit a somewhat complicated behavior if heat treatment is accompanied by oxidation. Cottonseed oil darkens when heated to a high temperature, and the color becomes "set," *i.e.*, impossible to remove by treatment with alkalies or bleaching earth.

Palm oil exhibits certain characteristics of behavior which may be ascribed to its high content of beta carotene. When the oil is hydrogenated even slightly, its deep orange-red color is replaced with a light yellow or yellow-red color similar to that of other refined vegetable oils. When it is heated to a high temperature, the original deep color disappears, and solid "break" material is precipitated. After reduction, the carotenoid pigments of palm oil do not regain their color as the oil becomes oxidized.[5a]

It is well known that carotenoid pigments are readily picked up by adsorbents. The yellow-red color of most vegetable oils is reduced without difficulty by treatment of the oil with bleaching earths or earth and carbon. However, oils from badly damaged seeds or animal tissues, which contain brown pigments evidently derived from decomposed proteins and carbohydrates, may be very resistant to bleaching by adsorption.

The fact that refined vegetable oils usually have a number of pigments and exhibit only general absorption in the red-yellow region, rather than definite absorption maxima, has thus far largely precluded any investigation of refining or bleaching in terms of the removal of any particular red or yellow pigment. On the other hand, green color in oils is apparently caused only by chlorophyll or related compounds, which have well-defined maxima at about 6600 Å. (chlorophyll A) or 6400 Å. (chlorophyll B). Consequently, the effect of various processing treatments on the chlorophyll content is known quantitatively. Pritchett and co-workers[6] found that a normal crude soybean oil with a chlorophyll content of 1000–1500 micrograms per liter (*ca.* 0.0001–0.00015%) had its chlorophyll content reduced about 25% by alkali refining, even though chloro-

[5] B. H. Thurman, *Ind. Eng. Chem.*, *24*, 1187–1190 (1932).
[5a] P. Dubouloz and S. Lalement, *Bull. mat. grasses inst. colonial M___ ___lle, 29*, 35–38 (1945).
[6] W. C. Pritchett, W. G. Taylor, and D. M. Carr___ ___ ___, *24*, 225–227 (1947).

phyll is ordinarily considered stable to alkalies and unstable to acids. By subsequent bleaching with acid-activated earth (prior to hydrogenation), it was possible to reduce the chlorophyll concentration to a very low value, e.g., 15 micrograms per liter. However, many processors prefer to give conspicuously green oils a light alkali treatment at a minimum temperature, followed by a heavy bleaching treatment. Although acid adsorbents are generally more efficient bleaching agents than neutral materials, the effect of acidity is particularly marked in bleaching to remove green color. Hinners and co-workers[7] have shown in a study of soybean oil bleached with five different earths that the bleaching efficiency is not determined by the "free" hydrogen or hydroxyl ion concentration of the earth, as calculated from the pH of an aqueous suspension, but is a function of the ion adsorption capacity, as measured by the difference between the "free" ion concentration and the concentration of titratable ion.

O'Connor and co-workers[7a] have recently published spectral absorption curves through both the visible and ultraviolet regions of crude cottonseed, soybean, peanut, sesame, rice bran, and okraseed oils, and of the same oils following the successive steps of alkali refining, adsorption bleaching, and steam deodorizing.

Limited hydrogenation gives the appearance of intensifying the green color of an oil, through its bleaching effect on the red and yellow pigments. However, Pritchett et al.[6] have shown that partial hydrogenation of a soybean oil (to an iodine value of 75) can be expected actually to reduce the chlorophyll content about two-thirds, and that substantially complete hydrogenation will reduce it to about 5% of its original value. Hydrogenation also appears to affect the chlorophyll chemically; in the case of soybean oil it causes the absorption maximum at 6600 Å. to shift to about 6400 Å., corresponding to a conversion of chlorophyll A to chlorophyll B.

Oxidation has an important effect upon the color of fats and oils. While oxidation bleaches the carotenoid pigments, it tends to develop the color of other types of coloring materials and in some cases apparently even produces colored compounds of a quinoid nature from the fatty acids or glycerides of the oil. The partial oxidation of vegetable oils causes an increase in their red and yellow color, most of which is apparently due to formation of the chroman-5,6-quinones described by Golumbic.[8] Cottonseed oil is particularly prone to darken upon oxidation (Fig. 89). Some lots of cottonseed and soybean oil darken so readily that the darkening tendency is noticeable in bleaching, poor bleach colors being obtained because of the development of new pigments parallel to the adsorption of old ones.

con··········thy, and R. E. Bass, *Oil & Soap*, *23*, 22–25 (1946).
········1, M. E. Jefferson, and F. G. Dollear, *J. Am. O*

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In a recent study of the bleaching of cottonseed and soybean oils, King and Wharton[9] have produced evidence that oxidation not only develops new pigments, but also stabilizes existing pigments against adsorption, with the adsorbent itself strongly catalyzing the oxidation reactions.

Inedible animal fats of high free fatty acid content may become very dark colored through reaction of their free acids to form colored compounds. Traces of iron and some other metallic contaminants greatly favor the development of dark colors in such fats.
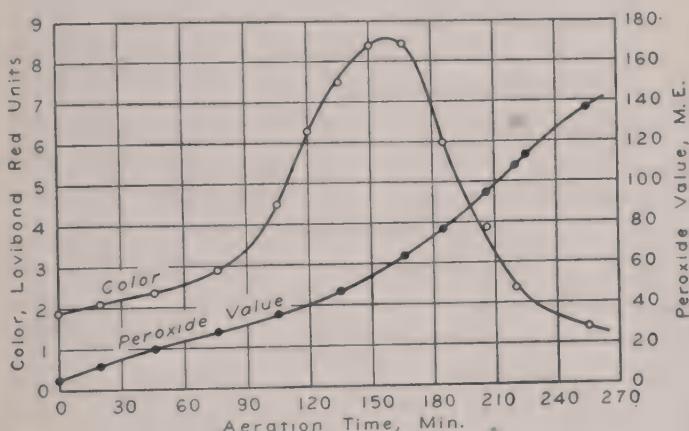
Fig. 89. Effect of oxidation (aeration at 120°C.) on the color of refined and bleached cottonseed oil.

Certain pigments, such as those in low-grade tallows and greases and in field-damaged soybean oil, are very refractory to ordinary refining and bleaching treatment, but may be removed effectively by liquid-liquid extraction.

Alkali refining with caustic soda removes a substantial, though minor, proportion of the sterols of vegetable oils; hence caustic soapstock is a good source of sterols.[10] Caustic refining has been reported[11] to remove as much as 10–20% of the tocopherols of soybean oil. Removal is presumably in each case by adsorption on the soap that is formed. Since free fatty acids and gums are largely eliminated by prior treatment with soda ash, the caustic soda soapstock from the second stage of the continuous soda ash-caustic soda refining process is said[2,12] to be particularly rich in both sterols and tocopherols. A minor proportion of both the sterols and tocopherols in oils is removed by steam refining or deodoriza-

[9] R. R. King and F. W. Wharton, *J. Am. Oil Chem. Soc.*, *26*, 201–207 (1949).
[10] See, for example, N. F. Kruse, E. B. Oberg, W. E. Mann, H. R. Kraybill, and K. E. Eldridge (one-half each to Central Soya Co. and Purdue R   Founda-tion). U. S. Pat. 2,296,794 (1942).
[11] H. W. Rawlings, N. H. Kuhrt, and J. G. Baxter
26 (1948).
[12] M. Mattikow (to Refining, Uninc.), U. S
(to Refining, Uninc.), U   313

tion. The amount in any case depends upon the severity of the process with respect to time, temperature, and stripping steam flow, and this varies greatly from one processor to another; very drastic deodorization is said[13] to be capable of reducing the unsaponifiable content of soybean oil by 30–60%.

Alkali refining may significantly reduce the vitamin A content of fish liver oils, through adsorption of the vitamin on the soaps formed *in situ* in the oil[14]; however, this is said to be obviated by refining in a solvent.[15] Chromatographic adsorption is a standard technique for the separation of tocopherols from oils, although ordinary bleaching with earths or carbon appears to abstract no significant amount of tocopherols. According to Buxton,[16] the treatment of fish liver oils with carbon removes antioxidants and renders the vitamin A in the oil unstable. Hydrogenation has no adverse effect upon tocopherols or other antioxidants, but saturates vitamin A and carotene and destroys their biological activity unless special precautions are taken.

Metallic contaminants in fats and oils are presumably in the form of metal soaps. Refining with caustic soda is effective in removing certain heavy metals; however, treatment of the oil with adsorbents appears to be a more certain method of removal. O'Connor and co-workers[17] found refining and bleaching more effective than refining alone for reducing the iron content of a hydrogenated cottonseed oil product, and refining and bleaching accomplished practically complete removal of nickel, whereas refining alone reduced the nickel content only from 10.1 to 6.7 parts per million. The "post bleaching" of oils after hydrogenation, to remove traces of nickel, is a common practice. In dealing with re-esterified oils containing zinc or tin catalysts, Feuge *et al.*[18] found that refining with caustic soda in 0.40% excess reduced the zinc content from 0.036% to 0.0001%, and that further treatment with bleaching earth reduced it to less than 0.00001%, whereas either refining alone or refining and bleaching reduced the tin content from 0.116% to less than 0.00032%.

A common method of removing metallic contaminants, which is particularly useful as an adjunct to the deodorization process is by means of so-called metal scavengers, or compounds which are capable of forming inactive complexes with iron or other heavy metals. The most popular compounds, which have been used in this country and abroad for many years, are certain acids, including phosphoric acid and organic acids such

[13] R. H. Neal (to Best Foods, Inc.), U. S. Pat. 2,351,832 (1944).
[14] H. N. Brocklesby, *The Chemistry and Technology of Marine Animal Oils*. Fisheries Research Board of Canada, Ottawa, 1941, p. 259.
[15] H. J. Passino, *Ind. Eng. Chem.*, 41, 280–287 (1949).
[16] L. O. ____, *Ind. Eng. Chem.*, 34, 1486–1489 (1942).
[17] R. ____, D. C. Heinzelman, and M. E. Jefferson, *J. Am. Oil Chem. Soc.*, 25, ____
[18] ____ and A. E. Bailey, *Oil & Soap*, 22, 202–207 (1945).

as citric and tartaric. Commercial lecithin is also effective at deodorizing temperatures, because of its phosphoric acid group. More recently, it has been demonstrated that certain polyhydroxy compounds, such as sorbitol and sugar or sugar derivatives are also metal scavengers.[19] The effect of metal scavengers and techniques for their use have been reviewed in recent articles by Dutton and co-workers.[20] In the series of experiments referred to above, Feuge et al.[18] found that treatment with strong phosphoric acid was as effective as refining and bleaching for tin removal, but that it was less effective with zinc, reducing the zinc content of the oil only to 0.0094%. Metal scavengers are particularly useful for eliminating contamination with iron.

Alkali refining itself introduces sodium soaps as a contaminant in oils. In general, European practice relies upon very thorough washing of the refined oil for soap removal, whereas in the United States it is felt that a low soap content is best insured by treatment with bleaching adsorbents and thorough drying of the oil during the bleaching operation, to reduce soap solubility. The analysis of oil for low concentrations of residual soap is somewhat uncertain, but it appears that in good practice the soap is reduced in bleaching to about 5–10 parts per million. Soap is strongly adsorbed by hydrogenation catalysts; hence hydrogenated oils are virtually free of this impurity. Spent catalysts are good adsorbents for soap; in processing soapy oils it may be advantageous to start the hydrogenation with a spent catalyst, adding an active catalyst later, with or without removal of the spent catalyst.

3. Refining Losses

Much of the technology of fat and oil refining is concerned with the minimization of oil losses, rather than the thoroughness of purification. In ordinary alkali refining with caustic soda there is always a considerable amount of neutral oil saponified by the alkali or entrained in the soapstock. This oil is recoverable only as a low-grade material, and hence it represents a direct monetary loss to the refiner.

The amount of neutral oil that is lost in alkali refining depends primarily upon the amount and kind of impurities in the oil. It is relatively low in the refining of such oils as coconut oil and palm kernel oil, and animal and marine fats, which are low in phosphatides and similar impurities. In the kettle refining of coconut oil, for example, the total loss usually does not exceed about 1.4 times the amount of free fatty acids removed. On the other hand, vegetable oils such as cottonseed and soy-

[19] A. K. Epstein, H. L. Reynolds, and M. L. Hartley, U. S. Pat. 40,793–794 (1938).
[20] H. J. Dutton, A. W. Schwab, H. A. Moser, and Chem. Soc., 25, 385–388 (1948); 26, 441–444 (1949).

bean oil can seldom be refined batchwise with a loss less than 3.0 times the free fatty acids content, even when the oil is relatively free of impurities; and more commonly the refining loss of low-acid oils is 5 to 10 times as great as the free fatty acids content.
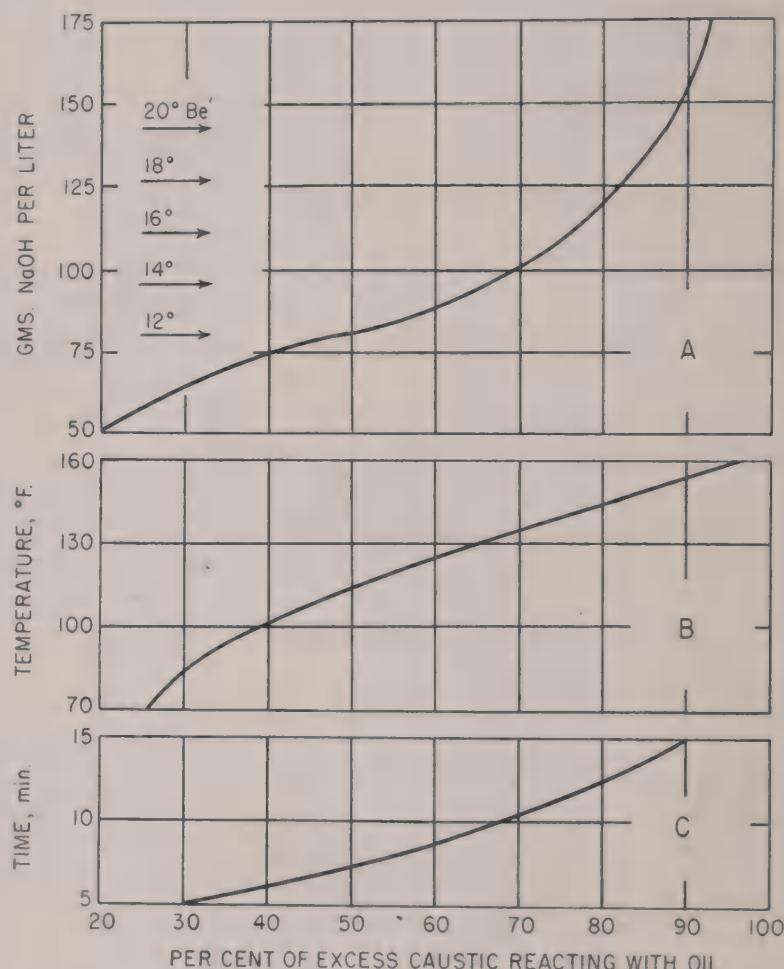
Fig. 90. Effect of: (A) strength of lye, (B) temperature, and (C) contact time, on the completeness of reaction of caustic soda solution with neutral oil. Values are in terms of percentage of total available caustic reacting under the following conditions: (A) temperature, 130°F., contact time, 10 min.; (B) contact time, 10 min., 14.1° Bé. lye; (C) temperature, 130°F., 14.1° Bé. lye. 0.153% excess NaOH used in all cases.

High refining losses in vegetable oils free from solid material are generally attributed to the presence of phosphatides. Possibly other gummy and surface active materials assist in emulsifying neutral fat and contribut.... .sses. However, it is to be noted that some impurities

tend to produce a hard soapstock and a low refining loss.[21] Gossypol, which may be present in crude cottonseed oil under certain conditions, is well known as a material which has a beneficial effect in refining,[22] and it has been shown[23] that other phenolic substances not found in crude oils similarly reduce the refining loss. The composition of a crude oil with respect to surface-active constituents is determined, of course, in the extraction process, and particularly during the cooking of the seed.

The newer continuous alkali-refining processes have been designed to reduce the loss of neutral oil by saponification as well as by entrainment in the soapstock. It is to be noted that neutral fats and oils are actually quite resistant toward reaction even with quite strong lyes and that a small amount of caustic soda solution mixed into a neutral oil will undergo substantially complete reaction only after a somewhat prolonged period at an elevated temperature. This is shown clearly by the data published by Thurman,[23a] which are reproduced in Figure 90. The three curves in the figure show the effect of lye strength, temperature, and contact time on the saponification of neutral oil, in terms of the percentage of the total excess caustic reacting, i.e., the excess of caustic above that required to react with 0.075% of free fatty acids. The lye used in each experiment contained sufficient sodium hydroxide to neutralize the free acids, plus 0.153 gram per 100 grams of oil, or a sufficient amount, if totally reacted, to saponify 1% of the neutral oil.

In the refining of oils by other techniques, as for example by steam distillation or liquid-liquid extraction, the question of neutral oil loss by saponification or entrainment of course does not enter.

A method was developed by Wesson[24] and modified by Jamieson[25] whereby an estimate could be made of the total amount of fatty acids and other substances which are normally removed from an oil by alkali refining. The content of these substances in the oil, often referred to as the "absolute loss," or the "Wesson loss," is of some significance in refining theory and practice, inasmuch as it represents a minimum value beyond which the refining loss of the oil cannot be reduced. The Wesson loss in crude cottonseed, soybean, peanut, and corn oils is ordinarily from 1–3% greater than the free fatty acid content of the oil. In a recent study of the Wesson loss on 39 hydraulic cottonseed oil samples and 29 expeller soybean oil samples, King and Wharton[26] found the Wesson loss of the

[21] See J. J. Ganucheau and E. L. D'Aquin, Oil & Soap, 10, 49–50 (1933).
[22] H. D. Royce and F. A. Lindsey, Ind. Eng. Chem., 25, 1047–1050 (1933). A. I. Skipin and M. Sokolova, Masloboino Zhirovoe Delo, 10, No. 8, 4–11 (1934).
[23] M. S. El'gort and N. V. Ionova, Masloboino Zhirovoe Delo, 12, 548–549 (1936).
[23a] B. H. Thurman, J. Am. Oil Chem. Soc., 26, 580–583 (1949).
[24] D. Wesson, J. Oil & Fat Ind., 3, 297–305 (1926).
[25] G. S. Jamieson, Vegetable Fats and Oils. 2nd ed., Reinh_ _ork, 1943, p. 454.
[26] R. R. King and F. W. Wharton, J. Am. Oil Ch_

cottonseed oil to average 1.70% higher than the free fatty acids content, and the Wesson loss of the soybean oil to average 3.31% higher. Extremes were 0.7–2.7% and 1.4–6.4%, respectively. The cottonseed oil samples varied from 0.9 to 2.8% in free fatty acid content and from 3.4 to 9.4% in refining loss by the official A.O.C.S. laboratory cup method, and the soybean oil samples varied from 0.5 to 1.4% in free fatty acids, and from 4.3 to 12.3% in refining loss.

Recently, Linteris and Handschumaker[26a] have described a simple chromatographic method for crude vegetable oils which appears to give a more accurate measure of neutral oil than the Wesson loss. It is more rapid and convenient than the Wesson method, and it yields an oil containing the normal refined oil pigments; consequently, the oil may subsequently be examined for color and subjected to a microbleaching test.

4. APPLICATIONS

Some oils and fats are seldom given any kind of purifying treatment. Butterfat, oleo oil, and olive oil are neither refined nor bleached in the ordinary course of manufacture, although upon occasion the refining process may be applied for the reclamation of off-grade or badly deteriorated materials.

Most of the lard on the market is not refined in the proper sense of the term. The product known to the trade as "refined lard" has merely been clarified and solidified, with the application of a light bleaching treatment, in some cases, by means of a bleaching clay or carbon. A few special lard products which are hydrogenated or deodorized are also alkali-refined. Small amounts of tallow or oleo stock are consumed without being refined, and considerable quantities of unrefined oleostearine are used in the manufacture of blended type shortenings and margarines of the "puff-paste" type. Inedible animal fats used in the manufacture of soaps are in some cases refined and in other cases unrefined. In the treatment of soap fats refining is chiefly valuable because of its beneficial effect on the color of the fats. Soap fats are almost invariably bleached.

In some parts of the world, particularly in Africa, Southern Europe and the Orient, considerable quantities of oil seeds yielding a relatively pure oil, such as peanut, sesame, rapeseed, and soybean, are cold-pressed, and the resulting oil is used for edible purposes, like olive oil, without further processing treatment. Oils which are to be deodorized and marketed as neutral salad or cooking oils, as well as vegetable oils which are to be converted into shortenings or margarines, are almost invariably alkali-refined. Free fatty acids are objectionable in all of these products, because of their tendency to cause smoking when the fat is heated. The

26a L. Linteris and Handschumaker, J. Am. Oil Chem. Soc., 27, 260–263 (1950).

higher fatty acids are so insoluble as to be practically tasteless; hence oils containing large proportions of these may be rendered at least temporarily neutral by deodorization alone. The fatty acids of coconut oil and other lauric acid type oils are sufficiently soluble, however, to taste strongly; it is therefore essential that these oils be rendered substantially free of free acids before they are used in food products.

Vegetable paint oils are not always alkali-refined, since in these oils a moderate content of free acids is unobjectionable. They are frequently acid- or water-washed to remove material which would precipitate under heat treatment. The removal of this so-called "break material" is essential in varnish oils, which are usually refined with alkali.

Whale, fish, and other marine oils, with the exception of fish liver oils, are refined before they are manufactured into edible products, since such products are invariably hydrogenated and deodorized. Fish liver oils are preferably not alkali refined because of the tendency toward vitamin A adsorption of soaps formed *in situ* in the oil.

B. Desliming or Degumming

As used here, the terms desliming and degumming refer to refining treatment that is designed to remove phosphatides and certain other ill-defined "slimes" or "mucilaginous materials" from the oil, but which does not reduce the acidity of the oil.

1. Degumming by Hydration

If oils intended for use in edible products are to be degummed, this is almost always accomplished by hydrating the phosphatides, etc., to make them insoluble in the oil.

Crude soybean oil, particularly that obtained by solvent extraction, is very often degummed before refining. As mentioned previously, gums, if left in the oil, tend to produce high refining losses and occasion trouble from settling out in storage tanks and tank cars; in addition, the gums, after reasonably simple and inexpensive refining treatment, are marketable as commercial soya lecithin. Other vegetable oils, such as corn, sunflowerseed, and peanut, also yield gums suitable for conversion to commercial lecithin; however, the market is generally well supplied by the standard soybean oil product, and hence in the United States these oils are less commonly degummed than soybean oil. The degumming of crude cottonseed serves to reduce the refining loss, but there is at present no market for the dark-colored resinous gums; the process is therefore generally considered uneconomic.

It is desirable for degumming to be completed before 2. shipped or placed in storage, and in addition, a bet from

fresh oil; degumming is therefore usually carried out at the oil mill or extraction plant rather than at the refinery. In all cases, separation of the hydrated gums from the oil is accomplished with continuous centrifuges similar to those used for the separation of soapstock in continuous refining. In some extraction plants the gums are allowed to hydrate from steam condensed in the last stage of steam stripping for removal of solvent from the miscella; in others, a small proportion of water (ca. 1%) is mixed continuously into the substantially dry oil. The minimum quantity of water consistent with a free-flowing product is desired, as any excess of water tends to make the separated gums ferment more readily, and, in any case, it must be removed from the final lecithin product. It is possible to obtain gums containing as little as 20–25% water. There is a small quantity of oil occluded with the gums, and hence there is a slight loss over and above the amount of impurities separated. A typical soybean oil will yield about 3.5% of material consisting of 25% water and 75% oil-soluble; the latter will contain about one-third oil and about two-thirds acetone-insoluble (phosphatides, etc.). If lecithin is to be reclaimed, the oil should, of course, be free of meal or other solid material before it is hydrated. As hydrating agents, in place of water, weak boric acid[27] and sodium chloride[28] solutions have been recommended, particularly for the degumming of cottonseed oil. A number of other reagents are suggested in the patent literature.[28a]

According to Kantor[28b] the content of foots or gums in linseed oil varies directly with the specific gravity of the oil (from 2.0% at a specific gravity of 0.9340 to less than 0.2% at a specific gravity of 0.9315). This permits the optimum amount of hydrating water (equal to the foots content) to be determined without difficulty. The dosage of water is said to be rather critical, inasmuch as the gums bind water within very specific limits.

Degumming is not ordinarily applied to animal fats, as these are very low in phosphatides. However, dry-rendered fats which have been produced with excessive dehydration of the parent tissues and which consequently are dark colored from the presence of proteinaceous matter can sometimes be lightened by a hydrating treatment.

Temperatures for degumming are not highly critical, although separation of the hydrated gums occurs more readily if the viscosity of the oil is reduced by operating at 90–120°F.

[27] B. H. Thurman (to Refining, Inc.), U. S. Pat. 2,201,063 (1940).
[28] B. H. Thurman (to Refining, Inc.), U. S. Pat. 2,150,732 (1940).
[28a] See H. Schönfeld. ed., Chemie und Technologie der Fette und Fettprodukte. Vol. II, Springer, Vienna, 1937, pp. 22–24.
[28b] M. Kantor J. Am. Oil Chem. Soc., 27, 455–462 (1950).

2. Preparation of Commercial Lecithin

The conversion of soybean oil gums to the various grades of commercial lecithin has been described by Langhurst[29a] and by Stanley.[29b] Material from the degumming centrifuges is charged into a dehydrating kettle equipped with a jacket for the circulation of hot water, and is agitated at 150–160°F. under a 28-inch vacuum until its moisture content is reduced below 0.5%. After centrifugal clarification, it is drummed for shipment. According to Stanley,[29b] the six common commercial grades consist of plastic-consistency and fluid-consistency products, each of which may be unbleached, single-bleached, or double-bleached. Bleaching is accomplished usually with hydrogen peroxide, which may be added either during the degumming step with the water used for hydration, or in the bleaching kettle. The fluid-consistency product is made by adding 2–5% of mixed soybean oil fatty acids or other free fatty acids to the plastic-consistency material. Specifications call for a minimum content of acetone-insoluble material of 65% and 62% for the plastic and fluid grades, respectively; for phosphorus contents of 2.2% and 2.1%, respectively; for nitrogen contents of 0.9% and 0.8%, respectively; and for maximum moisture and ether-insoluble contents of 1.0% and 0.2%, respectively, in all cases. Maximum acid values are 20% for the plastic grade and 30% for the fluid grade. The Lovibond color (5.25-inch column) of a 1% solution in colorless mineral oil must not exceed 30 yellow, 2.5 red for unbleached lecithin; 20 yellow, 1.5 red for single-bleached lecithin; or 10 yellow, 0.5 red for the double-bleached product. The special confectioners' product, from which soybean oil has been removed by extraction with acetone and replaced with cocoa butter, is now said to be in relatively little demand.

3. Acid Refining

The following procedure is recommended by Schönfeld[30] for the acid refining of crude vegetable oils such as linseed or rapeseed oils. For the operation, lead-lined kettles with conical bottoms and efficient mechanical agitators are used. Into the cold oil in the kettle, sulfuric acid of 66° Bé. strength is slowly mixed; with stronger acid there is danger of sulfonating the oil to an excessive degree. Care is taken to avoid raising the temperature of the mixture above 30°C. (86°F.). As the acid is added, the oil turns a greenish yellow, and later the charge darkens as impurities

[29] (a) L. F. Langhurst, Chapter XV, in *Soybeans and Soybean Products*, K. S. Markley, ed., Interscience, New York, 1950. (b) J. Stanley, *ibid.*, Chapter XVI.
[30] H. Schönfeld, ed., *Chemie und Technologie der Fette und Fettprodukte*. Vol. II. Springer, Vienna, 1937, pp. 17–18.

begin to separate in the form of small brown or black flocs. Samples are periodically withdrawn and examined on a porcelain plate, and as soon as there is a clean separation of flocculent material and clear oil, the addition of acid is stopped. The amount of acid required depends upon the individual oil, but is usually in the range of 0.5–1.5%.

Immediately after all the acid is added, 1–2% of hot water is mixed in, to dilute the acid and terminate its action, and the charge is allowed to set quietly until the water and acid layer has settled to the bottom and can be drawn off and discarded (overnight settling is usually required). The operation is completed by washing the oil about three times with hot water.

The loss in acid refining is confined essentially to the amount of gums removed, i.e., about 1.5–2.5% with most oils. However, the method appears to be decreasing in popularity, at least in the United States.

4. Removal of Break Material by Heat Treatment

Heat treatment is seldom ,if ever, employed alone for the removal of phosphatides or "break material" from oils. However, the heat treatment incidental to the steam refining process will cause the precipitation of such material.

C. Alkali Refining

The technology of alkali refining is concerned with the proper choice of alkalies, amounts of alkalies, and refining techniques, to produce the desired purification without excessive saponification of neutral oil, and with methods for the efficient separation of refined oil and soapstock.

In general, it may be said that the art of refining is much more elaborately developed in Europe and in areas influenced by European practice than it is in the United States, because of the greater variety of oils handled by European processors and the necessity in Europe for dealing with much oil that is of poor quality and difficult to refine properly. On the other hand, American practice in the rapid and continuous refining of cottonseed and soybean oils of good quality has reached a high degree of perfection and an efficiency that is unmatched by European batch methods. Recently, much interest has been manifested in continuous refining in Europe and in other places outside the United States, with the installation of many plants of American design, and the development of at least one new process of European origin.

1. Refining with Caustic Soda

(a) Selection of Lye

The selection of the proper amount and strength of lye for refining is highly important in the case of any oil or fat which is to be refined with caustic soda. It might be supposed that the lye to be used could be quite simply determined upon the basis of the free fatty acid content of the oil, but such is by no means the case. While a relatively pure fat like lard can be expected to exhibit a more or less predictable behavior in refining, according to its free acid content, the presence of pigments and surface-active substances in most vegetable oils makes their reaction to alkali treatment extremely variable. In addition to differences in the oil produced by different mills, due to variations in methods of processing the oils seeds, there are also well-defined variations in the characteristics of oils according to their geographical origin, and other variations according to climatic conditions, which occur from season to season. Variability in the reaction of the oil to refining and bleaching is particularly marked in the case of cottonseed oil.[31]

TABLE 107

SODIUM HYDROXIDE CONTENT OF LYES OF DIFFERENT DEGREES BAUMÉ[a]

Degrees Baumé at 15°C.	Sodium hydroxide content, %
10	6.57
12	8.00
14	9.50
16	11.06
18	12.68
20	14.36
22	16.09
24	17.87
26	19.70
28	21.58
30	23.50

[a] American Oil Chemists' Society, *Official and Tentative Methods.*

In the choice of both lyes and refining methods, the refiner is invariably[31] guided by preliminary refining tests conducted in the laboratory. The official laboratory refining methods developed under the auspices of the American Oil Chemists' Society[32] and adopted by various trade organiza-

[31] See A. E. Bailey, ed., *Cottonseed and Cottonseed Products.* Interscience, New York, 1948, pp. 369–370.
[32] American Oil Chemists' Society, *Official and Tentative Methods,* V. C. Mehlenbacher, ed., 1946 (revised annually).

TABLE 108

TABLE FOR THE CALCULATION OF LYES FOR REFINING

A. Percentages of lyes of different strengths required to neutralize the free fatty acids in oils of varying acidity (free fatty acids calculated as oleic)

Free fatty acids, %	Per cent lye of Baumé strength:				
	12°	14°	16°	18°	20°
0.6	1.07	0.90	0.77	0.67	0.59
0.7	1.24	1.05	0.90	0.78	0.69
0.8	1.42	1.20	1.03	0.89	0.79
0.9	1.60	1.35	1.16	1.00	0.89
1.0	1.78	1.50	1.29	1.11	0.99
1.1	1.95	1.65	1.41	1.23	1.09
1.2	2.13	1.80	1.54	1.34	1.19
1.3	2.31	1.95	1.67	1.45	1.29
1.4	2.48	2.10	1.80	1.56	1.39
1.5	2.66	2.25	1.93	1.67	1.49
1.6	2.84	2.40	2.06	1.79	1.58
1.7	3.02	2.54	2.18	1.90	1.68
1.8	3.20	2.69	2.31	2.01	1.78
1.9	3.37	2.84	2.44	2.12	1.88
2.0	3.55	2.99	2.57	2.23	1.98
2.1	3.73	3.14	2.70	2.35	2.08
2.2	3.91	3.29	2.83	2.46	2.18
2.3	4.08	3.44	2.96	2.57	2.28
2.4	4.26	3.59	3.08	2.68	2.37
2.5	4.44	3.74	3.21	2.80	2.47
2.6	4.61	3.89	3.34	2.91	2.57
2.7	4.80	4.04	3.47	3.02	2.67
2.8	4.97	4.19	3.60	3.13	2.77
2.9	5.15	4.34	3.72	3.24	2.87
3.0	5.32	4.49	3.85	3.36	2.97
3.2	5.68	4.78	4.10	3.58	3.16
3.4	6.04	5.18	4.35	3.80	3.36
3.6	6.39	5.48	4.61	4.03	3.56
3.8	6.75	5.78	4.87	4.25	3.76
4.0	7.10	6.08	5.12	4.47	3.95
4.2	7.45	6.38	5.38	4.70	4.15
4.4	7.80	6.68	5.64	4.92	4.35
4.6	8.16	6.98	5.89	5.15	4.55
4.8	8.52	7.28	6.15	5.37	4.74
5.0	8.88	7.47	6.42	5.60	4.94

TABLE 108—*Concluded*

B. Percentages of lyes of different strengths required to provide different
excesses of lye (excess calculated as dry sodium hydroxide)

Excess, %	Per cent lye of Baumé strength:				
	12°	14°	16°	18°	20°
0.05	0.62	0.53	0.45	0.39	0.35
0.10	1.25	1.05	0.90	0.79	0.70
0.15	1.87	1.58	1.35	1.18	1.05
0.16	2.00	1.69	1.44	1.26	1.12
0.17	2.12	1.79	1.53	1.34	1.19
0.18	2.25	1.90	1.62	1.42	1.26
0.19	2.28	2.00	1.71	1.50	1.33
0.20	2.50	2.10	1.81	1.58	1.39
0.21	2.63	2.21	1.90	1.66	1.46
0.22	2.75	2.31	1.99	1.74	1.53
0.23	2.88	2.42	2.08	1.81	1.60
0.24	3.00	2.52	2.17	1.89	1.67
0.25	3.13	2.63	2.26	1.97	1.74
0.26	3.25	2.73	2.35	2.05	1.81
0.27	3.38	2.84	2.44	2.13	1.88
0.28	3.50	2.94	2.53	2.21	1.95
0.29	3.63	3.05	2.62	2.29	2.02
0.30	3.75	3.15	2.71	2.37	2.09
0.31	3.88	3.26	2.80	2.44	2.16
0.32	4.00	3.36	2.89	2.52	2.23
0.33	4.13	3.47	2.98	2.60	2.30
0.34	4.25	3.57	3.07	2.68	2.37
0.35	4.37	3.68	3.16	2.76	2.44
0.36	4.50	3.78	3.25	2.84	2.51
0.37	4.62	3.89	3.34	2.92	2.58
0.38	4.75	3.99	3.43	3.00	2.65
0.39	4.88	4.10	3.58	3.07	2.72
0.40	5.00	4.21	3.61	3.15	2.79
0.41	5.13	4.31	3.70	3.23	2.86
0.42	5.25	4.42	3.80	3.31	2.93
0.43	5.38	4.52	3.89	3.39	3.00
0.44	5.50	4.63	3.98	3.47	3.06
0.45	5.63	4.73	4.07	3.55	3.13
0.46	5.75	4.84	4.16	3.63	3.20
0.47	5.88	4.85	4.25	3.70	3.27
0.48	6.00	4.95	4.34	3.78	3.34
0.49	6.13	5.16	4.43	3.86	3.41
0.50	6.25	5.26	4.52	3.94	3.48

tions (see page 530) serve not only to evaluate shipments of crude cotton-
seed oil and other oils, on the basis of their worth to the refiner, but also
provide a close indication of the results to be expected from comparable
treatment of the oil in the plant. Thus, by refining samples of an oil with
different amounts and strengths of lye, and with different times of stirring,
etc., and noting the refining loss and color of the oil obtained in each case,
it is possible to determine the optimum conditions for refining the oil in
the plant.

It is customary to measure the strength of lye solutions for refining in
terms of their specific gravity expressed in degrees Baumé. The refiner
ordinarily employs one of a series of lyes ranging from about 10° to 30°
Bé., in 2° steps, with oils of good quality usually being refined with 12°,
14°, or 16° lye. The actual sodium hydroxide content of lyes of different
strengths is shown in Table 107.

Ordinarily, the refiner uses lye containing a sufficient amount of sodium
hydroxide to produce the color desired in the oil, and uses the strength of
lye which will produce the lowest refining loss with the desired color. In
general, the best results are obtained with relatively weak lyes on low free
fatty acid oils, and with stronger lyes on high acid oils, but the exact lye
to be used in any case can be determined only by trial. American refineries
customarily calculate the amount of lye required to neutralize the free
fatty acids in the oil, and to this amount add an excess depending upon the
characteristics of the oil. The excess is expressed in terms of dry sodium
hydroxide, on a percentage basis, calculated on the weight of the oil. Table
108 gives the percentages of lyes of various strengths which are required
to neutralize different percentages of free acids in the oil, and also the
additional amounts of lye required to provide sodium hydroxide in differ-
ent degrees of excess. The use of the table may be made clear by an ex-
ample. Thus, it may be desired to know the percentage of 16° lye required
to refine an oil containing 2.0% free fatty acids, with 0.45% excess so-
dium hydroxide. Referring to the table it will be seen that the neutraliza-
tion of 2.0% free acids, calculated as oleic, requires 2.57% of 16° lye.
An excess of 0.45% corresponds to 4.07% of the same lye. The total
amount of lye required is the sum of the two, or 6.64%.

Animal and marine fats of good quality and coconut oil or other
vegetable oils very low in gums and pigments may usually be refined sat-
isfactorily with 0.10–0.20% excess sodium hydroxide. Other vegetable
oils and low-grade animal fats require sodium hydroxide in increasing
excess as their content of gums and mucilaginous materials increases, and
as the necessity for decolorizing becomes greater. Cottonseed oil, for ex-
ample, is seldom refined with less than about 0.25% excess, and the use of
0.50–0. ᵇᵢ   is not uncommon, even in dealing with oils of rela-
tive   ᵗⁿᵃ   ᶜᵒⁿ   mounts of lye specified for official laboratory

refining tests by the National Cottonseed Products Association[33] for cottonseed, peanut, corn, and coconut oils, and by the National Soybean Processors Association[34] for soybean oil may be considered more or less representative of good refining practice, although in many cases substantially less lye may be used, particularly if the color of the refined oil is not a prime consideration. For good hydraulic cottonseed oil containing 0.5–1.0% free fatty acids, the prescribed excess of sodium hydroxide (in the form of 12° or 14° Bé. lye) is about 0.45%. For oils of increasingly poorer quality greater excesses and stronger lyes are specified, with the minimum excess rising to 0.74% (14° and 18° Bé.) at 4.0% free fatty acids, and to 1.28% excess (20° and 26° Bé.) at 15.0% free fatty acids. Good expeller soybean oils are tested by refining with two different amounts of 12° lye, with the sodium hydroxide excess amounting to about 0.35% and 0.58% excess in the two cases, and with little change in the excess specified for oils up to 5.0% in free fatty acids. Extracted soybean oil is refined similarly with 14° lye, with the corresponding excesses being about 0.35% and 0.50%. The preceding applies only to soybean oil that has not been degummed. Degummed soybean oil is given two test refinings, with 12° lye and with 0.10% and 0.20% excess sodium hydroxide, respectively, regardless of the acidity of the oil.

The official refining methods for peanut oil specify 12° and 16° Bé. lyes for peanut oils not over 3.0% in free fatty acids, and 16° and 20° lyes for poorer oils; excesses of sodium hydroxide vary from 0.25 to 0.47% for the better oils, and do not exceed 0.55% for oil with 10.0% free fatty acids. For corn oils, 16° lye is specified in all cases, with excesses of about 0.25 and 0.36% for the better oils. The official refining test method specifies for coconut oil the use of 20° Bé. lye only, with the amount used being in all cases approximately one-tenth greater than that theoretically required to neutralize the acidity of the oil, calculated in terms of oleic acid. Actually, the average molecular weight of coconut oil fatty acids is only about three-fourths that of oleic acid, and hence the real excess is nearly one-half the amount of lye required for neutralization, rather than one-tenth.

In proposing a standard refining and bleaching test for evaluation of the inedible tallows and greases used by soapmakers, Parsons[35] has suggested the use of 20° Bé. lye, with the excess of sodium hydroxide being 0.20% when the free fatty acids content does not exceed 4.0%; 0.30% when it is greater than 4.0% but not over 6.0%; 0.50% when it is greater than 6.0% but not over 8.0%, and 0.60% when it is 8.0 to 15.0%.

[33] National Cottonseed Products Association, *Rules Governing Transactions Between Members, 1949–1950*, Memphis, 1949 (issued annually).
[34] National Soybean Processors Association, *Yearbook and*, 1949–1950, Chicago, 1949 (issued annually).
[35] L. B. Parsons, *Oil & Soap*, *20*, 256–257 (1943)

In the alkali refining of linseed oil and other drying oils for the manu-
facture of paints and varnishes, Touchin[36] recommends that the excess
of lye be adjusted according to the content of "break material" found in
the oil as the result of a heating test.

Drying oils are generally refined with somewhat less excess lye than
edible oils.

As will be explained later, it is sometimes necessary to use salt, sodium
carbonate, or other electrolyte in conjunction with caustic soda, to insure
adequate salting or graining out of soapstock. Sodium silicate has often
been used with caustic soda in the refining of oils yielding sloppy foots, to
"weight" the foots and promote their settling.

(b) Batch Refining by the Dry Method

The dry method of refining is the one generally practiced in the United
States where any edible fat or oil is to be refined by means of caustic
soda. This method is termed "dry" because the oil is treated with a rela-
tively strong lye, and the soapstock or "foots" are recovered in a solid or
semisolid form, from the cooled oil. It is distinguished from the "wet"
method of refining, in which the soapstock is washed to the bottom of the
refining kettle with considerable quantities of water, and recovered in
the form of a fluid solution. Dry refining has the advantage of being rapid
and convenient, and of producing a concentrated soapstock and a refined
oil relatively free of soap or moisture. It is particularly adapted to the
refining of cottonseed oil, which in most cases produces a firm soapstock,
free from any considerable amount of occluded oil. It is less suitable for
treatment of oils such as linseed or degummed soybean oil, which produce
soft, sloppy foots that do not readily settle to a firm mass.

The equipment required for batch refining is simple, consisting of an
open tank or kettle, equipped with an agitator, steam coils for heating,
and a conical bottom. It is common for refining kettles to hold a full tank
car of oil, or 60,000 pounds. The agitator consists almost invariably of a
central vertical shaft, to which are attached a series of horizontal paddle
arms; the latter are placed in staggered positions down the shaft, so that
they will reach all portions of the kettle charge, and are inclined at an
angle of 45°, to give a lifting action when they are in motion. Common
agitator speeds are about 40 r.p.m. for rapid agitation and 8 r.p.m. for
slow agitation; the former must be sufficiently vigorous to bring about
intimate mixing and emulsification of the oil and lye, whereas the latter
is designed only to keep the contents of the kettle moving, and to main-
tain particles of soap in suspension in the oil while they undergo melting
and coalescence.[37]   Many refiners prefer continuously variable speed

[36] F. . . . . con . . . . . r Chem. Assoc., 28, 49–54 (1944).

drives, although two-speed drives are common, and appear to be satisfactory for most purposes. The heating coil must be designed to bring up the temperature of the batch rapidly; usually, but not always, the cone of the kettle is steam-jacketed, to assist in melting and discharging of the foots after refining is completed.

The first stage of refining is carried out with the oil at atmospheric temperature, or in the case of a fat, at a temperature only high enough to keep the material molten and liquid. Higher temperatures are avoided, partly because they tend to increase the amount of neutral oil saponified, but more because lighter refined oil colors are obtained at relatively low temperatures. For the refining of cottonseed oil, where color removal is particularly important, an initial temperature of 68–75°F. is preferred and specified for the official laboratory refining tests, although no marked disadvantage appears to result from a temperature up to about 90°F. If the oil contains occluded air after it is pumped to the refining kettle, it must be settled long enough for the air to rise to the surface and escape, as otherwise the foots will entrain sufficient air to float partially, and thus will not settle properly to the bottom of the kettle.

After the charge of oil is at the proper temperature, and free from air, the agitator is started at high speed, and the proper amount of lye is rapidly run in. The lye is usually distributed fairly evenly over the surface of the oil, although an elaborate distribution or spraying system is not necessary. Agitation is then continued until the alkali and oil are thoroughly emulsified. With some oils the best results are obtained if the mixing period is relatively short, e.g., 10 to 15 minutes. Other oils, of the "slow-breaking" type, may be mixed as long as 30 to 45 minutes. At the end of the mixing period the agitator is reduced to a low speed, sufficient only to keep the contents of the kettle stirred, and heat is applied to bring the temperature of the charge up to 135–145°F. as rapidly as possible. Under the influence of the heat, the emulsion breaks, and the soapstock separates from the clear oil in the form of small flocculent particles which tend to coalesce as stirring is continued. After the desired degree of "break" is obtained, agitation is stopped, heat is turned off the kettle, and the soapstock, or foots, is allowed to settle to the bottom of the kettle by gravity. Thorough settling of the soapstock before the oil is drawn off is essential if the refining loss is to be low. With cottonseed oil or other oil that has a high refining loss or a tendency for much neutral oil to be occluded in the soapstock, a settling time of about 10–12 hours is minimum, and the batch is usually settled overnight. On the other hand, oils such as lard or tallow can be refined quite satisfactorily with a settling time of 1–4 hours.

[37] C. B. Cluff, *Oil & Fat Inds.*, *4*, 168–171 (1927)

When the contents of the kettle are well settled, the refined oil is drawn off the top, through a swinging suction pipe, leaving the soapstock in the form of a more or less coherent mass at the bottom. Usually, two suction lines of different sizes are provided, of which the larger is used to remove the bulk of the oil, and the smaller is used for a final skimming operation. Removal of the last portions of oil, by judicious use of the suction pipe, and by manipulating the foots with a pole or paddle, requires considerable skill on the part of the operator. If the amount of soapstock is large, a portion is usually dropped through a large quick-opening valve in the bottom of the cone, into an open soapstock-receiving tank under the kettle, before skimming is completed. In many plants, the skimmings are not mixed with the bulk of the refined oil, but are diverted to a separate tank or kettle, where they are again settled. The soapstock, too, is often heated and skimmed for oil recovery, in the soapstock receiver. However, a dark-colored oil is obtained, which must be re-refined.

Although dry refining produces a relatively clean and clear oil, the refined oil nevertheless contains traces of moisture and soap that should be removed before the oil is put into storage. As a cleaning-up procedure, a common practice is to filter the refined oil through spent bleaching earth. The use of spent earth, already saturated with oil, avoids loss of oil through retention on the earth. If the oil is bleached before it is stored, it is of course dehydrated and freed of soap in the bleaching operation.

The above procedures are not essentially altered if the fat to be refined is tallow or other animal fat, although the entire operation must, of course be carried out at a temperature above the solidifying point of the fat.

Much care must be exercised in the refining of oils containing excessive proportions of free fatty acids, i.e., above 15–20%. Unskillful treatment of such an oil may result in the saponification of so large a proportion of the charge that it will be impossible to effect a separation of the foots and the oil. In some cases it may be advisable to refine high-acid oils in two stages, with only partial neutralization being accomplished in the first stage. Generally, poor oils of very high acidity can be handled more satisfactorily by some variation of the wet refining method, to be described below.

(c) Batch Refining by the Wet Method

In European refineries, where most of the oils refined are high in free fatty acids and produce soft soapstocks, the "wet" refining method is commonly practiced. In general it involves heating the oil charge to a relatively high temperature, e.g., 150°F., mixing in the lye, and washing down th̲e̲ ̲p̲r̲e̲c̲i̲p̲i̲t̲a̲t̲e̲d̲ soapstock with a spray of hot water directed onto the s̲u̲r̲f̲a̲c̲e̲.̲ ̲I̲n̲ ̲s̲o̲m̲e̲ ̲c̲a̲s̲e̲s̲,̲ salt, sodium carbonate, or other

electrolyte is added to assist in breaking the emulsion of soapstock and oil, and to aid in graining out and settling the soapstock. Several successive water washes are required to complete the substantial removal of soap from the oil. After each wash, the oil must, of course, be thoroughly settled. Innumerable variations of the method are practiced, according to the idiosyncrasies of the particular oil being processed, and little published information is available concerning the details of the method followed in different cases.

It is to be noted that the wet method is particularly advantageous for refining oils of very high acidity. For neutralizing extracted olive oil, which is said to average about 20% free fatty acids, Lewis[38] recommends one of the following alternative methods: (a) The oil is heated to 140–150°F. and emulsified with 10% of its own weight of water. Strong (45° Bé.) lye is then added in the calculated amount exactly to neutralize the free fatty acids, with agitation being discontinued and the soapstock being allowed to settle immediately after the lye is added. (b) The oil is heated to 125°F. with agitation, and sufficient 20° Bé. lye is added to combine exactly with the free acids. It is then heated to 135°F., 10–15% of 10% soda ash solution is added, heating is continued to 160°F., and agitation is stopped. It is reported that oils containing as high as 35% free fatty acids can be refined by these methods, with refining losses somewhat in excess of twice the free fatty acid content.

The wet refining method is little used in the United States, except for the refining of coconut or other lauric acid oil. Usually the oil, at about 150°F., is treated with 20° Bé. lye in sufficient amount to give about 0.10% excess sodium hydroxide, plus salt in the dry form or in the form of a strong brine, equivalent to about 0.10% sodium chloride per 1.0% free fatty acids in the oil. The salt is used because of the small excess of sodium hydroxide and the fact that coconut oil soaps require a relatively large concentration of electrolyte to cause them to grain out (see page 847). After a short period of agitation, the foots are washed down with hot water. Refining losses amount uniformly to about 1.4 times the quantity of free fatty acids neutralized. As the loss cannot be materially improved by any of the new continuous refining processes, virtually all coconut oil and similar oils are refined batchwise.

According to Kantor,[28b] in the batch refining of linseed oil, the oil is commonly treated according to a typical dry refining method, but after the soapstock has settled for 0.5 hour to 2 hours the batch is washed down with two successive 5% portions of water, and then after a final settling period of 12–24 hours under heat, the soapstock is drawn off in a fluid form.

[38] R. R. Lewis, J. Am. Oil Chem. Soc., 24, 315–316 (1948).
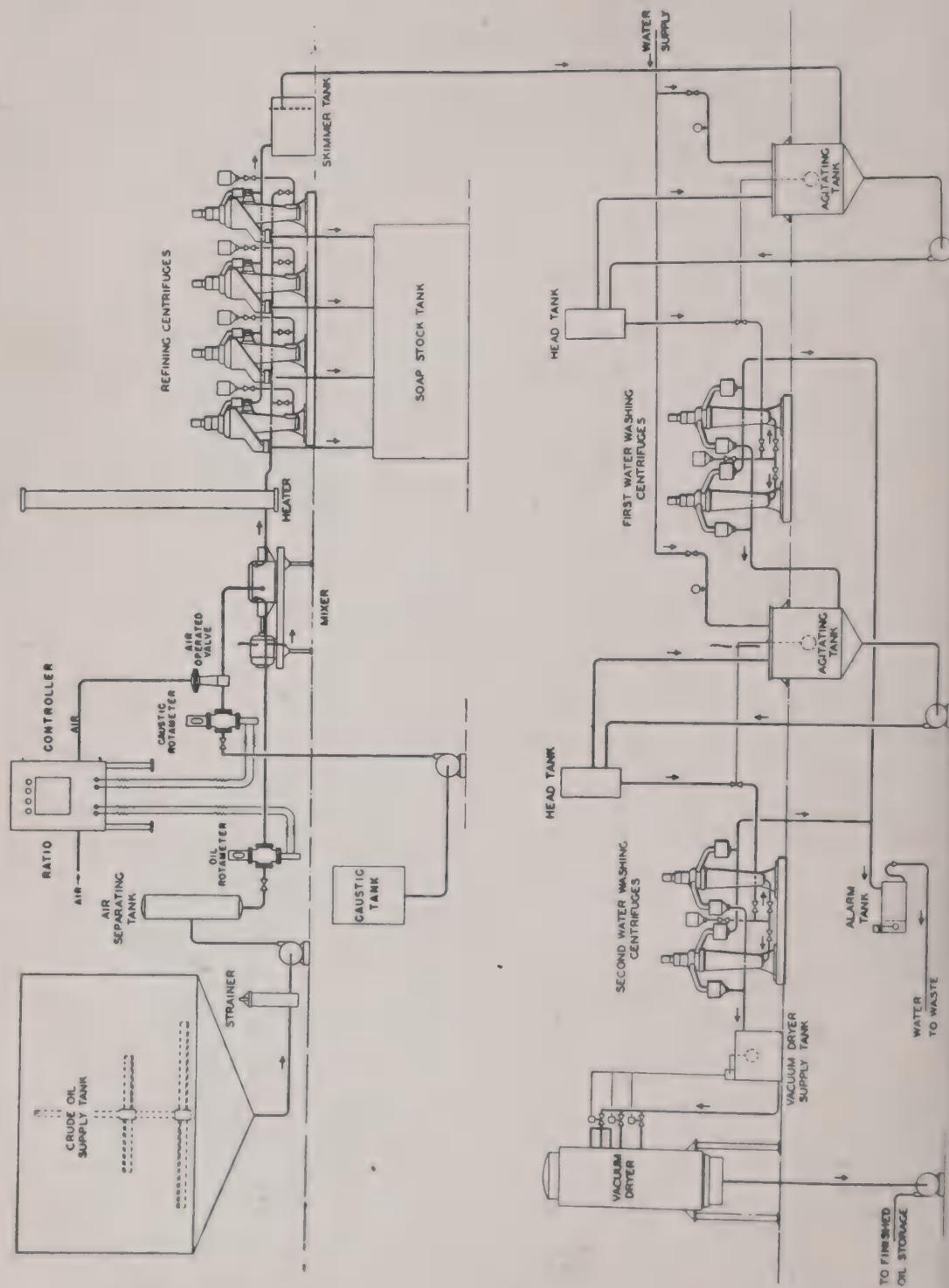
Fig. 91. Flow diagram, continuous continuous caustic soda refining plant (caustic oil separated)

Refining equipment for the wet method is not essentially different from that employed in refining by the dry method, except that it is quite common practice to use closed kettles, which may also serve as vacuum bleachers for the refined and washed oil.

(d) Continuous Caustic Refining

The batch method of caustic refining vegetable oils such as cottonseed and soybean has been largely superseded in the United States by continuous methods, in which the separation of oil and foots is carried out in centrifuges. The continuous method has the double advantage of greatly reducing the time of contact between oil and alkali, and effecting a very efficient separation of foots and oil. Consequently it reduces to a minimum the loss of neutral oil through saponification or occlusion in the soapstock, and at the same time produces a refined oil of equally as good grade as batch methods.

The first continuous plants installed in the United States for refining cottonseed oil were sold under a guarantee that they would effect a 30% saving in refining loss over kettle refining. A recent report by Tyler[39] (Table 109) indicates a slightly smaller average saving in the refining of oils now being produced.

Although centrifugal refining was proposed as early as 1923, by Hapgood and Mayno,[40] successful continuous systems were not developed until about 10 years later, as a result of the work of James[41] and of Clayton and Thurman and associates.[42] The first system installed in the United States was described by James[43]; the present process, embodying certain refinements, has been reviewed by Tyler,[39] from whom the following description is taken.

Crude oil from a feed tank (Fig. 91) is pumped continuously to a motor-driven mixer, where it is treated with a metered amount of caustic soda solution; a ratio flow controller is used to maintain a constant flow of caustic in relation to the flow of oil. The emulsion of lye and oil from the mixer passes through a low-pressure steam heater, where a break is obtained by raising the temperature to 140–160°F.; immediately thereafter the refined oil and soapstock are separated in a primary battery of high-speed centrifuges. From the centrifuges the soapstock drops by gravity into an elongated receiving tank, and the oil passes through a small tank where any foots accidentally entering the oil stream can be skimmed off, and

[39] L. D. Tyler, Food Inds., 20, 1456–1459 (1948).
[40] C. H. Hapgood and G. F. Mayno (to DeLaval Separator Company), U. S. Pat. 1,457,072 (1923).
[41] E. M. James (to Sharples Specialty Co.), Brit. Pat. 407,995 (1934); Fr. Pat. 743,449 (1933); Can. Pat. 355,720 (1936); U. S. Pat. 2,050,844 (1936).
[42] B. Clayton (to Refining, Inc.), U. S. Pats. 2,100,276 and 2,100,277 (1937), and succeeding patents. B. Clayton, W. B. Kerrick, and H. M. Stout (to Refining, Inc.), U. S. Pats. 2,100,274, 2,100,275 (1937); 2,137,214 (1938); 2,   ) T'   n (to Refining, Inc.), U. S. Pat. 2,150,733 (1939) and succeed
[43] E. M. James, Oil & Soap, 11, 137–138 (1934).

thence into a wash tank. The entire time elapsing between introduction of the lye and separation of the soapstock is only about three minutes.

TABLE 109

COMPARISON BETWEEN BATCH AND CONTINUOUS CENTRIFUGAL REFINING OF CRUDE COTTONSEED OIL[a]

Test No.	FFA of crude oil, %	Color, Lovibond red		Bleach color, Lovibond red		FFA content, %		Refining loss, %		Saving in loss by continuous refining, %
		Batch	Cont.	Batch	Cont.	Batch	Cont.	Batch	Cont.	
1	1.4	7.3	6.9	1.6	1.6	0.011	0.015	6.7	4.8	28.3
2	3.5	10.7	9.5	2.3	2.3	0.009	0.025	11.7	9.0	23.1
3	0.9	6.2	6.9	1.7	1.7	0.005	0.015	5.9	4.2	28.8
4	1.8	7.4	7.4	1.7	1.7	0.013	0.018	8.2	5.7	30.5
5	3.7	11.0	9.5	2.3	2.3	0.015	0.024	11.7	8.9	23.9
6	2.5	8.2	8.1	1.9	1.9	0.017	0.020	9.2	6.7	27.2
7	1.7	7.5	7.7	1.9	2.0	0.015	0.020	7.5	5.3	29.3
8	1.9	7.3	8.1	1.6	1.9	0.015	0.018	8.0	5.9	26.2
9	2.7	9.5	9.3	2.4	2.2	0.018	0.025	9.4	6.6	29.8
10	3.1	10.3	9.0	2.3	2.2	0.018	0.027	10.8	8.6	20.3
Average	2.32	8.5	8.2	2.0	2.0	0.014	0.021	8.91	6.57	26.3

[a] L. D. Tyler, *Food Inds.*, *20*, 1456–1459 (1948).

In the wash tank the oil is mixed continuously with 10–20% of hot water, with the temperature of the mixture being maintained at 160° to 180°F. Intimate contact of the water with the oil, to wash out small amounts of soap (usually 0.10–0.20%) remaining from the primary separation, is achieved by drawing the water–oil mixture from the bottom of the tank and rapidly recirculating it through a small "head tank" and back into the tank. The time of contact between the oil and water is about 10 minutes. From the head tank the mixture of oil and wash water is fed by gravity to a battery of secondary centrifuges which separate the water and dissolved soap from the washed oil. In some plants the oil is "double water-washed" in a second identical operation.

The wash water from the above operation passes through a safety tank or oil trap equipped with an oil flow alarm to the sewer. The washed oil goes to a small supply tank and from this tank is sprayed into a vacuum dryer maintained under an absolute pressure of about 1.5 inches of mercury by means of a two-stage steam ejector system with barometric condenser. Here, the moisture content, which may be as high as 0.5%, is reduced to 0.05% or less. From the dryer the refined, washed, and dried oil is pumped to further processing or to storage.

The continuous Sharples plant, described above, employs either hollow-bowl or disc-bowl centrifuges. The DeLaval plant is an essentially similar system which employs only disc-bowl centrifuges and relies upon proportioning and mixing devices of somewhat different design. The basic patents covering the process for both plants are held by Refining, Uninc.[42]

Recently, a new Short-Mix continuous caustic refining system has been announced by the European DeLaval company.[44] The distinctive feature of this system is a hermetically sealed centrifuge which permits the oil

Chemist, *25*, 349–358 (1949).

to be refined at a high temperature (75–90°C.), with a corresponding reduction in the contact time (about 10 seconds). Extremely low refining losses are claimed, although at the present writing (1950) no information is available concerning its performance in comparison with the system described above.

Mention has been made previously of the necessity for having the temperature of crude oil below about 90°F. when the lye is added, in order to obtain good refined oil colors in batch caustic refining. It should be stated here that this limitation does not apply to the same degree in the rapid continuous refining of oils, where in some cases much higher temperatures may be employed with entirely satisfactory results.[45]

An American process[46] which has been used commercially on a limited scale employs a special mechanical device to convert both oil and caustic to the form of a fine mist before they are reacted. The actual reaction time is but a small fraction of a second. Strong lyes (24–32° Bé.) are used, and a soapstock high in total fatty acids (60–65%) is obtained. It is claimed that in the re-refining of oils superior color reduction can be obtained by using but 0.2% of 32° Bé. lye, with the refining loss amounting only to about 0.5%.

(e) Re-refining

The dark-colored crude oils obtained from damaged vegetable oil seeds can be reduced to a reasonably light color more satisfactorily by means of a double refining than by employing an excessive amount of lye in a single refining. Off-grade cottonseed oils are usually refined first with a normal lye containing about 0.60–0.80% excess sodium hydroxide, and later, before bleaching, are re-refined with a smaller percentage of lye which is usually stronger than that employed originally. For some reason, a better reduction in color is obtained in many cases if the oil is stored for some time before re-refining, than if it is re-refined immediately. The following plant and laboratory experiments illustrate the beneficial effect of re-refining on the color of crude cottonseed oil, and also the improvement in color resulting from storing the oil after it is first refined. In these experiments, all plant refinings were carried out in continuous centrifugal equipment, and all laboratory refinings were conducted by the official A.O.C.S. method. Laboratory bleach tests were conducted by the official A.O.C.S. method, except that 4% of a commercial acid-activated bleaching earth was used, instead of 6% of the official earth. Color readings are by the A.O.C.S. method, on the Lovibond scale.

[45] B. H. Thurman, Proceedings of a Six-Day Short Course in Vegetable Oils, American Oil Chemists' Society, University of Illinois, 1948, pp 2,:
[46] R. H. Fash (to Anderson. Clayton & Co.), U. S. Pats,   ar   042 (1944). R. H. Fash, J. Am. Oil Chem. Soc., 24, 397–402 (19

The oil used in the tests consisted of a sample of crude cottonseed oil containing 5.0% free fatty acids. Refined in the laboratory, this oil yielded the following results:

> Lye used, 13.6% of 16° Bé.
> Refining loss, 12.3%
> Color of refined oil, 35 yellow, 10.9 red
> Bleach color, 35 yellow, 3.9 red

In the plant the oil was refined with results as follows:

> Lye used, 12.5% of 16° Bé.
> Color of refined oil, 35 yellow, 13.5 red
> Bleach color, 35 yellow, 5.1 red

Immediately after refining, samples of both the laboratory- and plant-refined oils were re-refined in the laboratory with 6.0% of 5° Bé. lye, with the following results:

> Color of laboratory-refined oil, 35 yellow, 10.9 red
> Color of laboratory-refined oil, re-refined, 35 yellow, 9.3 red
> Bleach color of above, 20 yellow, 2.7 red
> Color of plant-refined oil, 35 yellow, 13.5 red
> Color of plant-refined oil, re-refined, 35 yellow, 9.8 red
> Bleach color of above, 20 yellow, 3.1 red

The following samples were stored for 30 days at atmospheric temperatures during the months of May and June:

A. The laboratory-refined oil, filtered through paper to remove moisture.
B. The plant-refined oil, filtered as above.
C. The plant-refined oil, not filtered.
D. The crude oil.

At the end of the 30-day storage period, the free fatty acid content of the crude oil (Sample D) had increased to 5.3%. It was then refined in the laboratory with the following results:

> Lye used, 13.6% of 16° Bé.
> Refining loss, 12.2%
> Color of refined oil, 35 yellow, 12.1 red
> Bleach color, 35 yellow, 3.9 red

At the end of the 30-day period, samples A, B, and C were re-refined with 6.0% of 5° Bé. lye, results of the re-refining being as follows:

> Sample A, color of re-refined oil, 35 yellow, 7.7 red
>   Bleach color of above, 20 yellow, 1.7 red
> Sample B, color of re-refined oil, 35 yellow, 9.3 red
>   Bleach color of above, 20 yellow, 2.1 red
> Sample C, color of re-refined oil, 35 yellow, 9.3 red
>   Bleach color of above, 20 yellow, 2.1 red

con___ that storing the refined oil for 30 days resulted in
i__   ____h color of the laboratory-refined oil from

2.7 red to 1.7 red, and the color of the plant-refined oil from 3.1 red to 2.1 red.

Although, as indicated above, a substantial reduction in color may be obtained even with weak lyes, a strong lye is to be preferred for the maximum color reduction. Re-refining with a strong lye can be readily accomplished by the wet method, where the soap is washed down with a large amount of hot water, to produce a liquid soapstock. However, if the dry method is followed, *i.e.*, if a firm soapstock and a relatively clear oil is desired, special methods must be followed, which demand considerable skill and good judgment upon the part of the operator. A satisfactory method for cottonseed oil is described by James[46a] as follows.

The cold (75–80°F.) oil is agitated for 15–20 minutes at high speed with 1.0 to 1.5% of 40° Bé. lye. The agitation is then reduced and the temperature is raised to 130–140°F., after which hot (180–200°F.) water is sprayed onto the surface of the charge, with further reduction of the agitation. Very careful regulation of the amount of water added serves to soften the soap particles and produce a good break, without liquefying the soapstock. After all the water has been added, the operation is finished by agitating for 2–3 minutes at the lowest possible speed, settling, and drawing off the oil in the usual manner. Losses vary from 1.5 to 2.5%, depending upon the skill of the refiner.

Oils may be re-refined very satisfactorily with 20° Bé. lye through the second stage of the soda ash–caustic soda continuous refining equipment, which employs a hot-water flush to assist in the discharge of the soapstock. However, it is difficult to obtain a satisfactory separation of oil and soapstock in continuous equipment designed for straight caustic soda refining unless a somewhat weaker lye is used. The loss from continuous re-refining with soda ash equipment often is not more than 0.125%.

(f) Refining in a Solvent

There is at present considerable interest in the alkali refining of oils in the presence of solvents, particularly on the part of processors who operate solvent extraction or liquid-liquid plants, and thus produce an oil–solvent mixture in an intermediate stage of processing.

Alkali refining in a solvent has the great advantage of almost entirely avoiding loss of neutral oil to the soap phase, through either saponification or entrainment.[15,46b] According to Passino,[15] oils containing as much as 8–10% free fatty acids have been refined with caustic soda in liquid propane with the loss of less than 0.2% of neutral oil. The process is said to be highly advantageous in refining vitamin-containing fish liver oils,

[46a] E. M. James, Chapter XVII, in *Cottonseed and Cottonseed Products*, A. E. Bailey, ed., Interscience, New York, 1948.
[46b] B. Clayton (to Refining, Uninc.), U. S. Pat. 2,374,924 (

oils with a vitamin A potency of 30,000 units per gram having been re-
fined with the loss of less than 0.2% of the total vitamins to the soaps.

2. REFINING WITH OTHER ALKALIES

(a) Miscellaneous Reagents and Methods

Weak alkalies such as soda ash or sodium carbonate are capable of re-
ducing the free fatty acid content of crude oils or fats to a relatively low
value, or about 0.05–0.10% under favorable conditions, but they have
little effect upon color bodies. Nevertheless, there has in the past been
considerable interest in the use of weak alkalies, because they do not at-
tack neutral oil.

The carbon dioxide released by soda ash or other carbonate upon
reaction with fatty acids causes foaming and, in addition, entrainment of
the evolved gas in the soapstock prevents proper settling of the latter.
This, as much as the lack of decolorizing action, discourages the use
of carbonates in refining. However, carbonate refining in batch kettles
is feasible if special procedures are followed. Parsons,[47] for example, has
described a method for the refining of lard wherein the fat is treated
with sodium bicarbonate solution equivalent to two to three times the
content of free acids, after which the resultant soap is dehydrated by
heating and the removed from the fat by filtration, with the aid of
diatomaceous earth. It is said[47a] that the evolution of carbon dioxide may
be prevented by using a large excess of soda ash, under conditions that
lead to the formation of bicarbonate when neutralization of the fatty acids
occurs. In the highly successful Clayton continuous soda ash process, to be
described later, the soapstock is dehydrated and then rehydrated to
enable it to flow from the centrifuges.

In the refining by the dry method of oils that yield a soft soapstock,
a minor proportion of strong sodium silicate solution is sometimes added
to the lye, as this hardens and weights the soapstock and produces better
settling. However the use of silicate complicates acidulation of the
soapstock and some processors consider it difficult to remove with satis-
factory completeness from the oil.[48]

A recent patent[48a] covers the addition of a small amount (up to 0.75%)
of an inorganic phosphate, e.g., tetrasodium pyrophosphate, to oils prior
to refining with caustic soda, to reduce the refining loss.

Alkalies such as calcium and magnesium hydroxides do not reduce the

[47] L. B. Parsons (to Cudahy Packing Co.), U. S. Pat. 1,767,999 (1930).

[47a] E. Andre and P. Cuvier, Bull. mat. grasses inst. colonial Marseille, 29, 152–155
(1945).

[48] See J. W. Bodman, E. M. James, and S. J. Rini, Chapter XVII, in Soybeans
and Soybean Products. K. S. Markley, ed., Interscience, N. Y., 1950.

[48a] S.   . Rini   er Bros. Co.), U. S. Pat. 2,507,184 (1950).

color of crude oils effectively, and are seldom, if ever employed as re-
fining agents in commercial practice, although according to Thurman[5]
they may under certain special circumstances be advantageously used
in a dry form as bleaching agents.

Organic alkalies have been proposed from time to time for the refining of
crude oils, and patents covering the use of monoethanolamine have been
granted to Ashworth[49] and Hund and Rosenstein.[50] However, this agent
apparently has never come into commercial use.

(b) Clayton Soda Ash Process

The Clayton continuous soda ash process, which gives the oil succes-
sive treatments with soda ash and strong caustic soda, has been in com-
mercial operation since 1938 for the refining of cottonseed and soybean
oils, and in recent years has been widely adopted in American plants, and
to a lesser extent abroad, for the processing of a variety of oils.

The process has been described in articles by Mattikow[2,51] and Tyler.[39]
Using DeLaval equipment, it is carried out as follows: The crude oil is
pumped through a heat exchanger, where it is heated by a stream of
partially refined oil from another stage of the process, and then through
a steam heater, where its temperature is further raised to about 150°F.
It is then mixed with 20° Bé. (15.33%) soda ash solution. A single meter-
ing pump controls the flow of oil and soda ash solution, as well as that of
soda ash and caustic soda solutions used for subsequent steps of rehydra-
tion and re-refining.

For crude cottonseed or soybean oils containing more than 2.0% free
fatty acids, the amount of soda ash recommended for neutralizing is 1.5
times that required to react with the free fatty acids of the oil. For oils
of lower acidity, this amount plus 0.2% (dry basis) is recommended.
Additional soda ash may be required for oil very high in gums. Mixing
is carried out in a closed mechanically agitated vessel, with a steam
jacket; during the operation, the temperature is further raised to 210–
212°F. From the mixer the mixture is discharged to a dehydrator or vessel
maintained under about 28 inches of vacuum by a steam ejector with a
surface condenser, where carbon dioxide is removed and the moisture
content is reduced to 0.5% or less. To enable the dried soapstock to flow
from the centrifuges in the subsequent stage of separation, it is rehydrated
with about 3–7% of 20° Bé. soda ash (by volume, on the basis of the oil).
The amount of rehydrating solution required depends upon the charac-
teristics of the oil; it is kept at a minimum consistent with a satisfactory

[49] D. I. Ashworth (to DeLaval Separator Co.), U. S. Pat. 2,157,882 (1939).
[50] W. J. Hund and L. Rosenstein (to Shell Development Co.), U. S. Pat. 2.164,012 (1939).
[51] M. Mattikow, *Oil & Soap*, 19, 83–87 (1942).

separation, to produce a soapstock as high as possible in fatty acids. Mixing in of the rehydrating solution is accomplished in a second steam-jacketed mixer or series of mixers, and during the operation the temperature, which falls to about 160°F. in the dehydrator, is again raised to about 205°F.

The mixture of oil and rehydrated soapstock is separated in disc-bowl centrifuges, with the soapstock falling by gravity into a receiving tank, and the neutralized oil passing on to a surge tank. To assist in the discharge of soapstock from the centrifuges, about 1% by volume of 12° Bé. (8.57%) soda ash is introduced continuously into the centrifuge bowls.
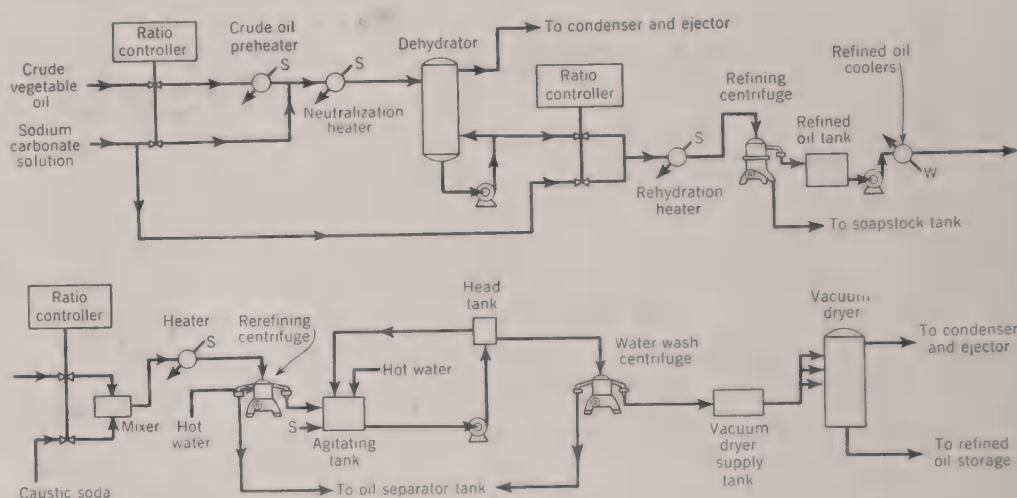
Fig. 92. Flow diagram continuous soda ash–caustic soda refining plant (courtesy *The Sharples Corporation*).

The soda-ash treated oil is free of gums and substantially neutralized (with a free fatty acid content of about 0.1%), but is usually quite dark in color. Further reduction of the acidity and the removal of color bodies is accomplished in a re-refining step using 20° Bé. caustic soda solution. Before re-refining, the oil, which is drawn from the surge tank, is cooled to about 160°F. in the case of soybean oil, or 80–90°F. in the case of cottonseed oil, with cooling being partially or wholly carried out by heat exchange with the crude oil entering the system. From 1 to 3% of 20° Bé. caustic soda is used as the re-refining agent; it is mixed with the oil in a mixer similar to those used for the first stage of refining and for rehydration, and in the process the temperature is raised to 140–160°F. The oil and soap phases are then separated in disc-bowl separators, with the soap discharging as a thin dark liquid. A stream of hot (200°F.) water amoun   con   10–20% by volume of the oil flow is used to flush the

centrifuge bowl. This water contacts only the soapstock; its function is
to dilute the latter sufficiently to prevent it from salting out into two
liquid phases. Stratification of the soap phase, with incomplete separa-
tion of the light phase and the oil, is prevented if the caustic soda solution
in the soapstock is diluted below about 8° Bé.[2] The caustic soapstock,
which carries with it very little of the free or combined fatty acids of the
oil, is discharged, along with the wash water, to the sewer. The re-refined

Fig. 93. Continuous soda ash–caustic soda refining plant. (Courtesy *The
Sharples Corporation*.).

oil is heated to 175–190°F., mixed with about 20% of wash water at
200°F., separated from the wash water centrifugally, and dried in a vac-
uum dryer, the operation throughout being continuous.

With Sharples equipment, the process is similar, except as modified by
differences in certain mechanical features. Both the Sharples and De
Laval plants operate under license of basic patents held by Refining,
Uninc.[52]

The chief advantage of the soda ash process is in the refining loss, which
with cottonseed, corn, and soybean oils runs 40 to 50% lower than in
batch refining, as compared with 20 to 30% lower for continuous refining
with caustic soda alone. Actually, the loss to be expected is indicated

[52] B. Clayton (to Refining, Uninc.), U. S. Pats. 2,190,593 and 2,. 594 (1940), and
succeeding patents

more accurately by the Wesson test (page 621); it is seldom greater than about 0.8% above the Wesson loss, and the difference is more commonly 0.4–0.6%. Some typical results, reported some time ago by the originators of the process, are shown in Table 110. In addition, the double refining treatment is said[45] to give consistently lower colors than can be obtained by a single caustic refining. It is also generally agreed that, while the equipment is more complicated than that used for straight caustic soda refining by the continuous method, it actually requires less skillful operation, as the quality of the refined oil, as well as proper separation in the centrifuges, is less sensitive to small variations in the characteristics of the crude oil.

TABLE 110

PERFORMANCE OF CLAYTON SODA ASH REFINING PROCESS[a]

Crude oil	FFA, %	Wesson loss, %	Plant loss, soda ash process, %	Official cup loss,[b] %
Cottonseed, Mississippi valley..	0.6	2.33	2.72	4.25
Cottonseed, Southeastern......	1.1	3.17	3.58	6.45
Cottonseed, Southeastern......	1.8	3.80	4.41	7.35
Corn oil, dry milled..........	1.24	2.34	2.5	4.9
Peanut oil..................	0.7	1.80	2.17	4.75

[a] M. Mattikow, *Oil & Soap*, *19*, 83–87 (1942).
[b] Official A.O.C.S. laboratory refining test method.

3. TREATMENT AND DISPOSAL OF SOAPSTOCK

While the soapstock or residue from alkali refining is a much cheaper product than the edible oil from which it is usually obtained, it nevertheless constitutes a valuable source of fatty acids for the soapmaker and fatty acid distiller. Of the two vegetable oils produced and refined in more accurately by the Wesson test (page 621); it is seldom greater than demand than that from cottonseed oil, as soybean oil fatty acids may be actually preferred to the oil for the manufacture of alkyd resins for the paint industry.

The value of soapstock is determined by its total (combined and free) fatty acids content, and this varies considerably according to the method of refining. Soapstock from batch refining seldom falls below 40% in total fatty acids, and often runs as high as 50%. The product from continuous caustic soda refining is usually between about 35 and 40% in total fatty acids. In refining by the continuous soda ash–caustic soda process, the total fatty acids content of the soapstock depends upon the amount of solution employed in the rehydrating step, and hence is quite variable. Very frequently, however, it is well below 35%. Jamieson[53] has

[53] G. S. Jamieson, *Vegetable Fats and Oils*. 2nd ed., Reinhold, New York, 1943, p. 206.

given the following composition for a typical cottonseed oil soapstock produced by kettle refining: moisture, 45.6%; neutral oil, 18.7%; fatty acids in the form of soap, 24.0%; ash as sodium oxide, 3.3%; and non-fatty substances, about 8%. According to Wurster et al.,[54] the ratio of neutral oil to fatty acids in the form of soap is about 2 to 5 in continuous caustic soda soapstock, and 1 to 4 in continuous soda ash–caustic soda soapstock.

From the refinery, soapstock is almost always shipped either in a raw form as it comes from the refining equipment, or in the concentrated form known as "acidulated" soapstock. Raw soapstock contains sufficient water to ferment readily. The official rules of the National Cottonseed Products Association[33] and the National Soybean Processors Association[34] provide for trading in the two commodities on the basis of a total fatty acids content of 50% and 95% for raw soapstock and acidulated soap-stock, respectively. Shipments of acidulated soapstock are rejectable if the total fatty acids fall below 85%; the corresponding minimum for raw soapstock is 35% under N.C.P.A. rules and 30% under N.S.P.A. rules. Soapstock from kettle or continuous caustic soda refining is frequently acidulated to reduce freight charges. Soapstock from continuous soda ash–caustic soda refining is acidulated for the same reason, and also, in many cases, to obtain a merchantable product.

Acidulation is accomplished by boiling the soapstock in an open tank or kettle with sulfuric acid, using open steam for heating and agitation. The tank must be acid-resistant; a common practice is to use a wooden tank with copper or bronze coils, lines, pumps, and fittings. The acid must be used in considerable excess; ordinarily the sulfuric acid is diluted to a strength of about 10%, and 8–12% of the dilute acid is added to the soapstock charge. After about 2–4 hours of vigorous boiling, the charge is allowed to settle for a short time, and the fatty layer is tested for total fatty acid content. If the latter is satisfactory, settling is continued over-night, or for a minimum of about 4–6 hours. If the total fatty acid content is low, as may happen with soapstock high in gums, additional acid is added, and boiling and settling are repeated. After the addition of acid is completed and the charge is well settled, the lower water and mineral acid layer, plus a certain amount of sludge, is run off to the sewer. The fatty material is then washed with one-fourth to one-half its own weight of water by boiling for a short time, settling overnight, and running off the wash water. One wash is usually sufficient to reduce the mineral acid content sufficiently to permit storage or shipment in ordinary steel tanks.

In a variation of the above process, some economy in acid consumption is achieved by skimming off the fatty layer and using the acid waters from the first boil to assist in the acidulation of the next batch. This method of

[54] O. H. Wurster, W. J. Govan, Jr., and G. J. Stockmann, Chapter XX in *Cotton-seed and Cottonseed Products*. A. E. Bailey, ed., Interscience 1948.

course requires additional tanks for washing or settling the material removed from the first tank.

The composition of acidulated soapstock depends upon the proportions of unsaponified oil and free caustic in the raw material. Usually, there is sufficient free alkali to saponify most of the neutral oil present, so that upon acidulation the fatty acids are largely converted to the free form. The free fatty acid content of an acidulated soapstock containing 95% total fatty acids is seldom below 80%, and is often 85–90% or more. If care is taken to have an excess of alkali, and the charge is well boiled before the acid is added, virtually all of the fatty acids may be liberated.

The utilization of soapstock by soapmakers and fatty acid processors has been described by Wurster et al.[54] and by Peterson.[55]   Soapstocks from the refining of coconut and other lauric acid oils are relatively light-colored and free of impurities, and can be used directly in some grades of laundry soaps. However, the products from oils such as cottonseed and soybean are dark-colored, malodorous materials which must undergo extensive purification before they are suitable for use even in cheap laundry soaps and washing powders. The first step in purifying soapstock in the soap plant consists of boiling the material with a slight excess of lye to insure complete saponification, followed by graining out of the soap in the form of a curd. The "spent lye" from this operation, containing 1.25–2.00% sodium hydroxide and 10–12% salt, is discarded, as the low ratio of neutral fat to free fatty acids in the charge and the presence of a high percentage of impurities makes glycerol recovery uneconomical. The curd, containing about 60% fatty acids, is mixed with a small proportion of water, and pumped to storage as "killed soapstock," where it may be held indefinitely awaiting further processing. When further processed, it is given a succession of alkali washes, and finally "finished" and settled into neat and niger phases, the various operations being identical with those carried out in processing any full-boiled stock (see pages 841–851).

Occasionally, the above operations or part of them are carried out at the refinery or by an intermediate processor. The product obtained by going through the washing operations, but finishing with a curd soap that is subsequently boiled down to a fatty acid content of about 65%, is known to the trade as "boiled down soapstock"; the product taken off in the form of a neat soap containing about 62% fatty acids is known as "settled soapstock." The latter is, of course, the purest product obtainable by kettle processing alone.

[55] W. A. Peterson, Proceedings of a Six-Day Short Course in Vegetable Oils, American Oil Chemists' Society, University of Illinois, 1948, pp. 132–141.

In general, raw soapstock tends to go to soapmakers and acidulated soapstock to fatty acid distillers, with, however, much of the distilled fatty acid product finding its way eventually into soap. When raw soapstock is purchased by distillers, it is acidulated promptly upon receipt.

The acidulated product, if high in combined fatty acids, must be split before it is distilled, to free the fatty acids from the neutral oil present. However, processors who refine and also distill, and thus have control of all operations, often find it advantageous to avoid the necessity of splitting by boiling the raw soapstock with a slight excess of added caustic before acidulation is carried out.

Distillation frees fatty acids derived from refining residues of their characteristic and objectionable odor more effectively than does any form of treatment in the soap kettle, and also accomplishes better color removal. Hence, it constitutes a preferable processing method for the soapmaker as well as for other users of fatty acids.

Although distillation practice has improved greatly in recent years, the production of light-colored acids from materials such as cottonseed oil soapstock is still something of a problem. A number of patents refer to methods of treating the fatty acids or the soapstock prior to distillation to improve the color or color stability. Sheely[56] describes a method of treating cottonseed oil fatty acids with hydrogen at an elevated temperature in the presence of a spent hydrogenation catalyst. McClain[57] claims that cottonseed oil soapstock boiled with an excess of caustic and then grained out, acidulated, and distilled, will yield lighter fatty acids if boiling is conducted in the presence of 0.05–0.50% potassium persulfate.

D. Other Refining Methods

1. Refining by Liquid-Liquid Extraction

Extraction of free fatty acids from oils with alcohols or other solvents with a greater affinity for free acids than for glycerides has often been proposed.[58] However, it is only since the introduction of the modern furfural and liquid propane (Solexol) processes that refining by liquid-liquid extraction has been practiced upon a large scale. As a refining method, it is particularly advantageous in dealing with inedible tallows and greases, field-damaged vegetable oils, or other very dark oils which

[56] M. L. Sheely (to Armour & Co.), U. S. Pat. 2,062,837 (1936).
[57] H. K. McClain (to Procter & Gamble Co.), U. S. Pat. 2,435,456 (1948).
[58] See, for example, H. Bollman, U. S. Pat. 1,371,342 (1921).

are difficult or impossible to bleach effectively by older methods.

The operation of a large commercial propane extraction plant for soap-makers' tallows and greases has recently been described by Moore.[59] Extraction of the fat at about 160°F., at a solvent ratio of about 17 to 1, in a single column without reflux, was found to concentrate most of the color bodies into a bottom or raffinate fraction amounting to about 2% of the feed. The material removed consists of pigments, oxidized fatty acids, and other undesirable constituents. Pilot plant tests have been reported[15] in which dark tallows and greases have yielded an oil with a Lovibond color as low as 10 yellow, 2.0 red (5.25-inch cell) with a 2% loss. In commercial operation it is said that taking off a 2% cut at a solvent ratio of 20:1 will reduce the Lovibond red color of tallow to 5–6, provided that its color is no darker than F.A.C. 45 originally. Propane extraction is said to be relatively ineffective for the removal of green color from tallow. In similar tests on vegetable oils the removal of a 2% raffinate cut reduced the color of crude soybean oil to 35 yellow, 3.0 red on the Lovibond scale, and removal of a 1.5% cut reduced the Gardner color of crude linseed oil from 11 to 4. Phosphatides and other impurities ordinarily removed by alkali refining also come out in the bottom cut, and oils such as soybean, cottonseed, or corn are suitable for immediate processing into edible products, provided that they are deodorized under conditions leading to effective removal of the free fatty acids, which are rather high in oil refined in this manner. Bodman et al.[48] have published a detailed discussion of propane extraction as applied to the refining of soybean oil.

By operating the propane process with three extraction towers and suitable reflux it is possible to obtain the bulk of an oil almost free from acidity, at the same time separating it into a low and a high iodine value fraction. In a typical pilot plant test cited by Passino,[15] crude soybean oil with an iodine value of 135, containing 0.4% free fatty acids, was separated into a first bottom cut of 2% (high in color bodies, as described above); a second bottom cut of 25% with an iodine value of 155 and 0.02% free fatty acids; a third bottom cut (edible fraction) of 72% with an iodine value of 128, a free fatty acids content of 0.04%, and a Lovibond color (5.25 inch cell) of 25 yellow, 2.5 red; and an overhead fraction of 1% containing most of the free fatty acids and unsaponifiable. The low iodine value soybean oil raffinate from the furfural extraction process, which ordinarily constitutes 30–40% of the feed and runs 110–120 in iodine value, is also low in color and free fatty acids (0.05% or below), and may be considered a fully refined oil.[60,61] At the present time (1950) there is apparently no commercial use of furfural extraction independently of glyceride fractionation for the refining of vegetable oils.

[59] E. B. Moore, J. Am. Oil Chem. Soc., 27, 75–80 (1950).
[60] S. W. Glover, Ind. Eng. Chem., 40, 228–236 (1948).
[61] S. W. Glover, J. Am. Oil Chem. Soc., 26, 162–166 (1949).

2. Steam Refining

Steam refining, or the removal of free fatty acids from oils by steam distillation, is frequently a useful method. The equipment and the technique are identical with those employed in modern high-temperature steam deodorization (Chapter XVIII), and often refining and deodorizing can be combined in one operation.

In general, steam refining is best applied to animal fats, well-degummed vegetable oils (other than cottonseed oil), or other fats and oils which are quite free of phosphatides or other break material (page 614). However, oils, e.g., palm oil, which "break" from the decomposition of carotenoids at high temperatures, may be steam-refined satisfactorily if the refining process is followed by treatment with a bleaching earth, or if the bulk of the free fatty acids is distilled out and the last portions (0.1–0.2%) are removed by alkali refining. The dark-colored material produced by the decomposition of phosphatides at high temperatures is very difficult to remove by refining or bleaching, and it also imparts an off-flavor to the oil. Steam refining has been used to a considerable extent in Europe on a variety of degummed vegetable oils, but in the United States it has thus far been widely used only in the refining of animal fats, where it is a standard method for reducing the free fatty acids of lard or mixtures of lard and edible tallow from 0.3–0.5% to 0.01–0.04% in the manufacture of animal fat shortenings.[62]

Losses in steam refining are usually lower than by any other method. With suitable equipment, mechanical loss of oil may be almost completely avoided; the distilled material consists, in addition to the free fatty acids removed, of a small amount of unsaponifiable material and neutral oil, including mono- and diglycerides. The exact amount, in any case, depends upon the composition of the oil, as well as its acidity. Ordinarily, in treating oils containing C_{16} and C_{18} acids, the neutral oil loss will not exceed about 0.5% in reducing the acidity to one-tenth of its original value. Hence, an oil containing 5.0% free fatty acids can, for example, be reduced to 0.05% free fatty acids with a refining loss not in excess of 6.0%.

Steam refining is recommended[15] as an adjunct to the single-column propane extraction process described above, where a low-acid product is desired.

3. Reduction of Acidity by Re-esterification

A number of proposals are to be found in the patent literature for reducing the free fatty acid content of oils by esterification, i.e., by reacting

[62] See, for example, A. E. Bailey, *National Provisioner*, October 30, 1948, pp. 10, 11, 23.

the oil with glycerol or monoglycerides to convert the free acids back to triglycerides.[63]   This method has apparently found limited commercial application in Europe, and in at least one case (for the treatment of extracted olive oil), its use has been reported in this country.[38]   It may be presumed to be useful only for highly acid oils, as glycerol cannot be made to combine with free fatty acids quantitatively, and esterification must be followed by other treatment, to decompose mono- and diglycerides and remove excess combined glycerol if this reagent is used in excess, or to remove a residue of free fatty acids if insufficient glycerol is used for complete esterification. As elevated temperatures are required for the reaction, the oil to be treated must presumably be free of gums.

E. Bleaching

1. COLOR STANDARDS

Among refiners in the United States the colors of the lighter refined and bleached oils, and also of shortenings and other oil and fat products, are usually determined by matching in a suitable tintometer a 5.25-inch column of the melted fat against red and yellow Lovibond color glasses. The red glasses are standardized by the National Bureau of Standards in terms of the Priest-Gibson N″ color scale.[64]   The N″ scale approximates, but does not exactly follow, the scale adopted by the manufacturers of the glasses.[65]   The latter, incidentally, varies slightly from one set of glasses to the other. Yellow glasses are not standardized, since relatively large variations in yellow are imperceptible to the eye, and in matching the color of a sample of oil it is only necessary to approximate the yellow color in order to obtain a satisfactory match with the red glasses.

For most purposes, and in the case of most oils, the depth of color of the fat or oil is satisfactorily expressed in terms of red units, according to the above scheme. The Lovibond system of color measurement is unsuitable, however, for oils which are excessively dark-colored or which contain in considerable strength color elements other than red and yellow. Among the vegetable oils which may contain colors other than red and yellow are olive oil, which generally has a greenish cast due to the presence of chlorophyll, and soybean oil, which may also contain considerable chlorophyll if expressed from green beans. Oils obtained from damaged oil

[63] See, for example, H. Schlink & Cie, Ger. Pats. 315.222 and 334.659 (1921); E. R. Bolton and E. J. Lush (to Technical Research Works Ltd.), Brit. Pat. 163,352 (1921) and U. S. Pat. 1,419,109 (1922); F. Gruber, Fr. Pat. 677.711 (1930); I. G. Farbenindustrie A.-G., Ger. Pat. 563,203 (1932).

[64] K. S. Gibson and F. K. Harris, Natl. Bur. Standards Sci. Papers No. 547 (1927). K. S. Gibson and G. W. Haupt, J. Research Natl. Bur. Standards, 13, 433–451 (1934); Oil & Soap, 11, 246–250, 257–260 (1934). H. J. McNicholas, Oil & Soap, 12, 167–178 (1935).

[65] I. G. Priest, Oil & Fat Ind., 6, No. 9, 27–29 (1929).

seeds are often brownish in color after refining, and hence are difficult or impossible to match with Lovibond glasses.

Because of the above-mentioned inadequacies of the Lovibond system, and also because of difficulties in obtaining suitable Lovibond glasses, American refiners have in recent years relied to an increasing degree upon the spectrophotometric evaluation of oil colors for both research and plant control work. Actually, the spectral transmission of an oil at 525–550 mμ is not only more reproducible than Lovibond red readings, but can also be closely correlated with the latter in the case of most oils. In 1950 a spectrophotometric method for the determination of oil color was adopted as a tentative method for refined and bleached vegetable oils by the American Oil Chemists' Society.[66] It provides for a determination of the optical density of the oil at 460, 550, 620, and 670 mμ in a 21.8-mm. cell, with the following equation being used for calculation of a photometric color which approximates color expressed in Lovibond red units:

$$\text{Photometric color} = 1.29\ D_{460} + 69.7\ D_{550} + 41.2\ D_{620} - 56.4\ D_{670}$$

Inedible tallows and greases are often too dark in color or too strong in green or other off-colors to be graded in terms of the Lovibond system, even when a short column, e.g., 1.25 inch, of oil is used. For the approximate evaluation of the colors of such fats, the Fat Analysis Committee of the American Oil Chemists' Society has provided an arbitrary system of color standards[67] consisting of sealed vials of solutions of various inorganic salts. The color of any fat in question is determined by comparing a melted sample with the various standards until the nearest match is obtained. The complete set of standards consists of 26 vials, numbered from 1 to 45, in odd numbers, and divided into five series. Numbers 1 to 9, inclusive, are prepared for the grading of light-colored fats; numbers 11, 11 A, 11 B, and 11 C are for very yellow fats; numbers 13 to 19 are for dark, reddish fats; numbers 21 to 29 are for greenish fats; and numbers 31 to 45 are for very dark fats. Spectral data on the various standards have been published by Urbain and Roschen.[68]

The above so-called F.A.C. color system is somewhat confusing, inasmuch as the different series of standards are to some degree independent, and thus there is not an orderly increase in color from the lowest to the highest numbered members of the set. Some of the standards numbered from 21 to 29, for example, may actually be lighter in color than standards numbered from 13 to 19. In addition, fats are often encountered

[66] See American Oil Chemists' Society Color Committee, G. W. Agee, chairman, *J. Am. Oil Chem. Soc.*, *27*, 233–234 (1950).

[67] American Oil Chemists' Society, *Official and Tentative Methods*, V. C. Mehlenbacher, ed., 1946 (revised annually).

[68] W. M. Urbain and H. L. Roschen, *Oil & Soap*, *16*, 124–126 (1939).

which do not match any of the standards. The F.A.C. colors are of course not additive.

Drying oils are commonly graded for color according to the Lovibond system or by matching with the 1933 Gardner color standards,[69] which likewise consist of solutions of inorganic salts and are numbered from 1 (the lightest) up to 18. The best pale commercial oils or bodied oils ordinarily have Gardner colors in the range of about 3 to 6.

Roughly, an F.A.C. color of 1 is equivalent to a Gardner color of 3, which is equivalent to a Lovibond color (5.25-inch column) of 27 yellow, 2.7 red. Other approximate equivalents among the lighter colors are as follows: F.A.C. No. 3 equals Gardner No. 5 equals Lovibond 70 yellow, 7.0 red; F.A.C. No. 5 equals Gardner No. 5 equals Lovibond 100 yellow, 10.5 red; F.A.C. No. 7 equals Gardner No. 9. A useful color conversion chart, which gives a comparison of color intensities among the above and other color systems, has been published by the Chemical Division of Armour & Co.[69a]

Certain grades of salad or cooking oils are purposely made rather dark, but the oil used in almost all other edible products is invariably reduced to a Lovibond red color of about 2.5 or below. Certain high-grade shortening products run consistently below 1.0 unit in red color. However, somewhat higher bleach colors are permissible, as considerable color reduction takes place in the operations of hydrogenation and deodorization. In general, the edible oil processor is concerned with bleaching to reduce the Lovibond red color of refined oils from about 4.0–9.0 to about 1.5 to 2.5 units, and at the same time remove green pigments almost completely if they are present. Soapmakers' fats are generally quite dark in color and required more drastic bleaching than do edible oils. The standards for bleaching vary greatly according to the product and its method of manufacture. In the manufacture of the better white soaps, color standards approach those of the edible industry, i.e., Lovibond red colors in the range of 5–6 units are required.

2. BLEACHING BY ADSORPTION

(a) Adsorbents

The most important adsorbent used in bleaching fats and oils is bleaching earth or clay. Natural bleaching earth, otherwise known as fuller's earth, from its ancient use in the "fulling" or scouring of wool, comprises various earths or clays consisting basically of a hydrated aluminum sili-

[69] H. A. Gardner. Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors. 10th ed., Inst. Paint and Varnish Research, Bethesda, Md., 1946.
[69a] Armour & Co., Chemical Division, The Handling, Sampling, and Testing of Fatty Acids. Chicago, 1947.

cate. The mineralogical characteristics of these earths have been discussed by Kerr[70] and Nutting.[71] Attempts have been made to correlate the chemical composition of earths with their bleaching ability, but without success. An earth almost devoid of adsorptive capacity may be almost identical in composition with very active earth; hence these materials can be evaluated only by actual tests. The earths used for bleaching fatty oils are the same as those used in a slightly different form and in much greater volume for the bleaching of petroleum products.

Within recent years natural bleaching earths have for use with fats and oils been supplanted to a considerable degree by acid-activated clays. The raw materials used for the manufacture of this type of bleaching clay consist for the most part of bentonites or montmorillonite which have little or no decolorizing power in the raw state.[72] By treatment with sulfuric or hydrochloric acid, however, the surface of the clay is so altered that its bleaching power will in most cases considerably exceed that of natural clays. The acid treatment undoubtedly extends the surface of the clay, and probably also causes important changes in its chemical or physicochemical nature. Acid-activated clays retain more oil per unit weight of clay than do natural earths, but their use generally leads to a lower over-all loss of oil through retention because of their greater activity. The apparent densities of natural earth, activated earth, and activated carbon are approximately 50 pounds, 45 pounds, and 30 pounds per cubic foot, respectively.

The activated clays are sold in neutral grades for bleaching edible oils and in slightly acid, but more active grades, for difficultly bleachable edible or inedible oils. The former, like the natural earths, do not materially increase the free fatty acid content of the oils upon which they are used, whereas the latter are inclined to hydrolyze the oil slightly, increasing its free acid content by a few hundredths of a per cent. Although the higher cost per ton of activated earths is usually compensated by their greater activity and the lower over-all loss of oil resulting from their use, so that they are often economical for bleaching ordinary high-grade edible oils, their greatest usefulness is in the treatment of off-grade oils. Certain types of color are extremely difficult to remove except by activated clays, e.g., as mentioned previously, the green color due to chlorophyll in some soybean oils is much more responsive to a slightly acid earth than one of the ordinary type because of the instability of this pigment under acid conditions.

Besides bleaching clay, the only adsorbent used to any extent on fatty oils is activated carbon. Because of its relatively high cost and its very

[70] P. F. Kerr, Am. Mineral., 17, 192–198 (1932).
[71] P. G. Nutting, U. S. Geol. Survey Circ. 3, 11, 17, 20 (1933).
[72] H. Odeen and H. D. Slosson, Oil & Soap, 12, 211–215 (1935).

high oil retention, carbon is not often used alone on most vegetable oils, but oil refiners frequently employ it in admixture with bleaching clay, in a ratio of about 10 to 20 parts by weight of clay to 1 of carbon. Such a mixture is often considerably more effective than bleaching clay alone. Carbon is very effective in removing the "bloom" caused by traces of mineral oil in vegetable oils, and is invariably used in the treatment of oils so contaminated. The merest traces of mineral oil may increase the apparent red color of an oil considerably. Fash[73] observed that 0.01% of fuel oil in crude cottonseed oil increased the refined and bleached color by as much as 0.7 Lovibond red unit, and 0.02% increased the color as much as 1.6 units. Carbon is also considered a superior adsorbent for traces of soap in refined oils. It is particularly effective in removing the red, blue, and green pigments of coconut and palm kernel oils and the better grades of animal fats, and is popular for use in connection with diatomaceous earth in clarifying and mildly bleaching lard.[74,75] Unlike bleaching earths, carbon imparts no foreign flavor or odor to the oil treated.

In bleaching most oils the cost of the adsorbent is exceeded by that of the oil lost by retention in the spent adsorbent. This oil is difficult to recover, and after recovery is usually badly oxidized and of poor quality; hence many refineries discard their spent earth without treatment. The retentiveness of an adsorbent is to some degree proportional to its activity, since both properties are related to the nature and extent of the adsorbing surface. The less active fuller's earths may not retain more than 20–25% of their own weight of oil, but acid-activated earths usually have a retention of 35–40%.[76] In the case of drying oils, which oxidize and polymerize more readily, the retention is normally higher, i.e., about 25–30% for natural earths and 40–45% for activated earths. Due to its very porous nature, carbon retains much greater amounts of oil than do any of the clays, and the addition of even 5 or 10% of carbon to a bleaching clay will materially increase the oil retention of the latter. The choice of an adsorbent depends in most cases upon striking a balance among the three factors of cost of the adsorbent, activity of the adsorbent, and oil retention.[77] Although laboratory bleach tests and retention tests will give some indi-

[73] R. H. Fash, *Oil & Soap*, *14*, 241–242 (1937).

[74] J. P. Harris, ed., *Active Carbon in the Decolorizing, Deodorizing, and Purifying of Oils, Fats, and Related Products*. Industrial Chemical Division, West Virginia Pulp and Paper Co., New York, 1944.

[75] A. B. Cummins, L. E. Weymouth, and L. L. Johnson, *Oil & Soap*, *21*, 215–223 (1944).

[76] For a laboratory method of evaluating the oil retention of bleaching earths, see A. S. Richardson, J. T. R. Andrews, and R. G. Folzenlogen, *Oil & Fat Ind.*, *6*, No. 9, 19–20, 43 (1929).

[77] For a discussion of the calculation of relative bleaching costs, with a nomograph, see R. B. Langston and A. D. Rich, *Oil & Soap*, *23*, 182–184 (1946).

cation of the value of a bleaching earth or carbon, it is necessary to resort
to tests on a large scale to evaluate these materials accurately. The un-
certainty in applying laboratory bleaching data to plant operations is in
marked contrast to the utility of laboratory refining tests, which furnish a
very reliable indication of the behavior of an oil in the plant.

The amount of adsorbent required for any given bleaching operation
will vary greatly with the activity and nature of the adsorbent, the variety
of oil, the color of the unbleached oil, and the color desired in the bleached
oil. In general, however, the amounts of bleaching clay used vary from
about 0.25% for lard to about 5% for dark-colored inedible tallows and
greases. Processors of edible cottonseed and soybean oil products ordi-
narily use about 1.0% of a high-grade earth. Carbon is not usually used
with such oils to the extent of more than about 0.2%, and then almost
always in conjunction with a bleaching earth.

(b) Theory of Adsorption Bleaching. General Considerations

Bleaching of oils by adsorption involves the removal of pigments which
are either dissolved in the oil or present in the form of colloidally dispersed
particles. From the standpoint of adsorption theory, it is immaterial
whether the pigments are dissolved or merely dispersed. The mechanics
of adsorption from such a system are somewhat controversial, there being
some difference of opinion as to the extent to which adsorption is physical
and the extent to which it is a chemical phenomenon. However, the
mechanics of the process need not be discussed here at length. It is suffi-
cient to recall that adsorption is a surface phenomenon, depending upon
a specific affinity between the solute and the adsorbent surface.

The capacity of an adsorbent for a dissolved material is directly related
to the concentration of the latter in the solution. As the concentration of
the solute decreases, there is a progressive and corresponding decrease in
the amount of solute taken up by a unit weight of adsorbent. The mathe-
matical expression relating adsorption to residual solute concentration at
a single temperature was developed by Freundlich,[78] and may be stated
as follows:

$$x/m = Kc^n$$

where x = amount of substance adsorbed, m = amount of adsorbent,
c = amount of residual substance, and K and n are constants. The above
equation may also be written in the form:

$$\log (x/m) = \log K + n \log c$$

[78] H. Freundlich, *Colloid & Capillary Chemistry*. Translated from the 3rd German
ed. by H. S. Hatfield, Methuen, London, 1926.

Thus it is apparent that a plot of x/m vs. c on a log-log scale will produce an adsorption isotherm which is a straight line, with a slope equal to n, and that x/m will be equal to K when c equals 1.

The Freundlich equation is valid for any method of color measurement, so long as the units of measurement are additive and proportional to the
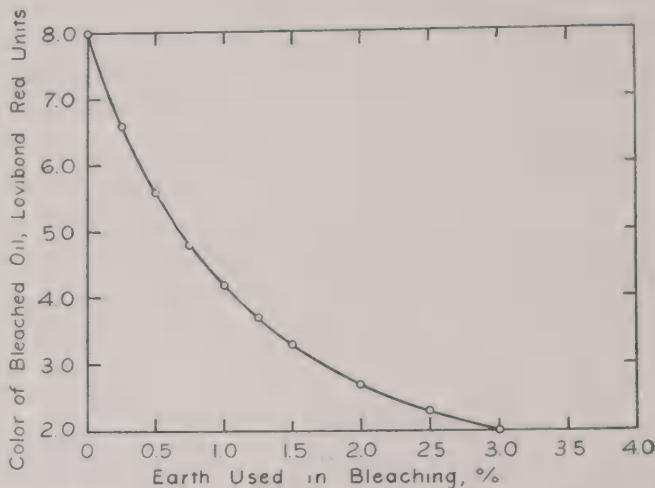
Fig. 94. Typical bleaching test on cottonseed oil (per cent earth used vs. bleach color of the oil).
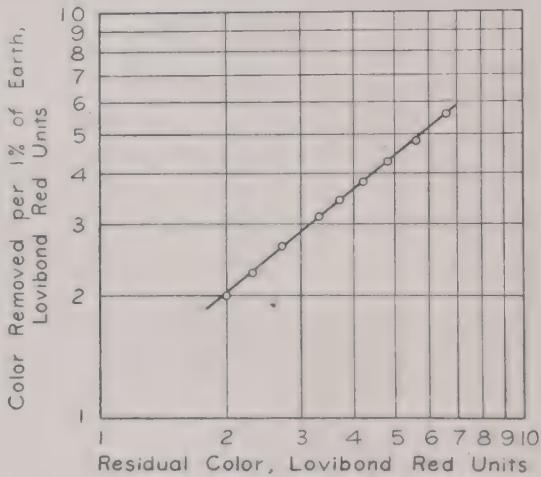
Fig. 95. Typical adsorption isotherm for the bleaching of cottonseed oil (same test as shown in Fig. 94).

actual concentration of coloring materials in the oil. In the case of fatty oils, either the Lovibond red color or the optical density at a specific wave length conforms to this requirement. Ordinarily (and throughout the following discussion), the unit weight of adsorbent, the quantity m in the equation above, is taken as one part per 100 parts of oil. With the

concentration of adsorbent so expressed, the adsorption isotherm and the values of K and n are independent of the units used for measuring color or pigment concentration.

Results of a typical test to determine the bleach colors produced by different percentages of an adsorbent are shown in Figure 94. In this test, the oil was a refined cottonseed oil with an initial red Lovibond color of 8.0 units, and the adsorbent was an acid-activated bleaching clay. The adsorption isotherm calculated from the results of the same test is reproduced in Figure 95. The value of K for this particular test was 1.14 and the value of n, 0.84.

From a practical standpoint, K may be considered a general measure of the activity or decolorizing power of the adsorbent, whereas n is an indication of its characteristic manner of adsorption. If two adsorbents have different capacities for adsorbing color, but adsorb in the same characteristic way, i.e., if they exhibit different values for K, but the same value for n, the relative amounts required to effect a given degree of decolorization will be in inverse proportion to the values of K. For example, if the following equations are found to apply to earths, A and B, respectively,

$$(A) \qquad\qquad\qquad x/m = 0.5\,c^{0.5}$$

$$(B) \qquad\qquad\qquad x/m = 1.0\,c^{0.5}$$

bleaching with earth A will require twice as much earth as bleaching with earth B, and this relationship will hold at any level to which decolorization may be carried.

The value of n determines the range of decolorization within which the adsorbent exhibits its greatest relative effect. If n is high, the adsorbent will be relatively effective in removing the first portions of color from the oil, but relatively inefficient as an agent for effecting a very high degree of decolorization. If n is low, the reverse will be true.

The hypothetical bleaching curves for adsorbents yielding different combinations of K and n reproduced in Figure 96 (page 662) illustrate the principles mentioned above. Under all circumstances it is desirable to use an adsorbent that gives a high value of K, corresponding to a low position of the bleaching curve on the figure. In general, a high value of n is also desirable, although not at the expense of a high value of K. It is to be particularly noted that an adequate comparison of two adsorbents cannot always be made without specifying the level to which decolorization is to be carried. In Figure 96, for example, it will be seen that adsorbent C is superior to B in bleaching down to a color of 2.1 units, but that below this color level, B is superior to C.

In the bleaching of fats and oils, values of both K and n vary widely

according to the adsorbent, the particular oil bleached, and the method of bleaching. Values recorded by different observers, principally in laboratory tests, are shown in Table 111. Ordinarily, bleaching of oil in the plant requires considerably less earth than bleaching of the same oil in the laboratory. The difference is in the so-called "press bleach," or addi-

TABLE 111

BLEACHING OF FATTY OILS BY MEANS OF ADSORBENTS; VALUES FOR K AND n IN THE FREUNDLICH EQUATION AS REPORTED BY DIFFERENT OBSERVERS[a]

Observer	Oil	Bleaching agent	Bleaching conditions	Method of color measurement	K	n
Hassler	Cottonseed	Natural earth	Lab. atmos.	Lovibond red units	0.6	0.45
and	Cottonseed	Carbon	Lab. atmos.	Lovibond red units	0.20	2.2
Hag-	Coconut	Natural earth	Lab. atmos.	Lovibond red units	0.5	1.3
berg[b]	Coconut	Carbon	Lab. atmos.	Lovibond red units	7.2	1.8
Bailey[c]	Cottonseed	Natural earth[d]	Lab. atmos.	Lovibond red units	0.6	0.4
	Cottonseed	Activated earth	Lab. atmos.	Lovibond red units	1.14	0.84
	Cottonseed	Activated earth	Lab. atmos.	Lovibond red units	0.90	0.34
	Cottonseed	Activated earth	Plant atmos.	Lovibond red units	1.6	0.73
King	Cottonseed	Natural earth	Lab. atmos.	Lovibond red units	2.0	0.42
and	Cottonseed	Natural earth	Lab. vacuum	Lovibond red units	3.3	0.39
Whar-	Cottonseed	Activated earth	Lab. vacuum	Lovibond red units	4.0	0.39
ton[e]	Soybean	Natural earth	Lab. vacuum	Lovibond red units	2.3	0.36
Hinners	Soybean	Activated earth	Lab. vacuum	Spectral, 660 mμ[g]	0.25	0.33
et al.[f]	Soybean	Activated earth	Lab. vacuum	Spectral, 660 mμ[g]	0.58	0.33
	Soybean	Activated earth	Lab. vacuum	Spectral, 660 mμ[g]	1.10	0.33
Sierra[h]	Tallow	Activated earth	Lab. atmos.	Spectral, 470 mμ[i]	0.66	0.77
Talc	Tallow	Activated earth	Lab. atmos.	Spectral, 520 mμ[j]	0.85	0.80
Stout	Cottonseed	Natural earth	Lab. atmos.	Spectral, 475 mμ[i]	0.29	2.21
et al.[k]	Cottonseed	Activated earth	Lab. atmos.	Spectral, 475 mμ[i]	0.45	2.16
	Cottonseed	Mg silicate	Lab. atmos.	Spectral, 475 mμ[i]	0.10	4.00
	Soybean	Natural earth	Lab. atmos.	Spectral, 475 mμ[i]	1.00	1.21
	Soybean	Activated earth	Lab. atmos.	Spectral, 475 mμ[i]	3.12	1.48
	Soybean	Mg silicate	Lab. atmos.	Spectral, 475 mμ[i]	1.26	1.70

[a] Concentration of earth expressed as parts by weight per 100 parts of oil.
[b] J. W. Hassler and R. A. Hagberg, Oil & Soap, 16, 188–191 (1939).
[c] A. E. Bailey, unpublished data.
[d] Official bleaching earth of American Oil Chemists' Society.
[e] R. R. King and F. W. Wharton, J. Am. Oil Chem. Soc., 26, 201–207 (1949).
[f] H. F. Hinners, J. J. McCarthy, and R. E. Bass, Oil & Soap, 23, 22–25 (1946).
[g] Measure of green color or chlorophyll content.
[h] Sierra Talc & Clay Co., Los Angeles, Cal., Leaflet AF-1, 1948.
[i] Measure of yellow color.
[j] Measure of red color.
[k] L. E. Stout, D. F. Chamberlain, and J. M. McKelvey, J. Am. Oil Chem. Soc., 26, 120–126 (1949).

tional decoloration as the oil passes through the bed of adsorbent retained in the filter press used for earth removal. Although no proof of the nature of "press bleaching" has ever been given, it may be presumed that it is a concentration effect leading to a new equilibrium between adsorbent and

pigments in the zone where the effective concentration of adsorbent is very high in relation to the oil.

It is evident from the Freundlich equation that bleaching clay or carbon which has reached equilibrium with respect to the coloring matter in a light oil will still have adsorptive capacity for the color in a darker oil. In other words, the greatest efficiency of bleaching will theoretically be attained in countercurrent operation, in a system wherein fresh oil is treated only with used adsorbent, and fresh adsorbent is brought into contact only with oil that has been partially bleached. True continuous countercurrent bleaching can scarcely be obtained with the adsorbent in the form of a powder, but it is possible to conduct the operation in a multiplicity of stages, with the adsorbent being moved from one stage to the other countercurrent to the movement of oil. With an infinite number of stages, the effect is, of course, equivalent to that of continuous countercurrent flow. Actually, the theoretical benefits are considerable even when the number of stages does not exceed two or three. Results obtained in the batch bleaching of certain vegetable oils in two countercurrent stages have been reported by Hassler and Hagberg.[79] In spite of its potential advantages, batch countercurrent bleaching is seldom practiced, principally because of the readiness with which oxidation of retained oil occurs when bleaching earth is exposed to the air in transferring the adsorbent from one stage to another. Countercurrent operation is more feasible in the continuous bleaching of oils within a closed system, and two-stage systems are actually in commercial use (see page 667). The advantage of countercurrent bleaching depends upon the curvature of the bleaching curve (Fig. 96), or in other words, upon the value of n, being greater the greater the curvature or the higher the value of n.

It can also be demonstrated, from the adsorption equation, that the application of an adsorbent in successive small portions should produce greater decolorization than the same amount of adsorbent applied in a single large dose. As in the case of countercurrent bleaching, the advantages in this method of operation should theoretically increase with increase in the value of n. However Odeen and Slosson[72] have reported laboratory tests with acid-activated clay in which multiple bleaching was less efficient than bleaching in which the entire amount of clay was added at one time. It appears probable that the prolonged heating and aeration to which the oil is subjected in such tests either converts the pigments to a difficultly adsorbable form, or develops new color through the production of new pigments, or the darkening of those previously present.

Unless bleaching is conducted with the rigid exclusion of oxygen, the normal color reduction brought about by the adsorption of pigments may have superimposed upon it effects due to oxidation which will consider-

[79] J. W. Hassler and R. A. Hagberg, *Oil & Soap*, *16*, 188–191 (1939).

ably modify the results. Reference has been made previously (page 616) to the darkening of oils from heating accompanied by oxidation. This effect appears to be accelerated in the presence of bleaching earth. On the other hand, it has been shown[80] that during the course of atmospheric bleaching tests of soybean oil in the laboratory, addition of earth before the oil is heated serves to inhibit heat darkening. This apparent anomaly is explained by King and Wharton[81] as a result of oxidative stabilization of pigments against adsorption; in other words, it may be assumed that addition of the earth early in the process enables it to adsorb pigments before oxidation occurs to reduce their affinity for the earth. Their theory
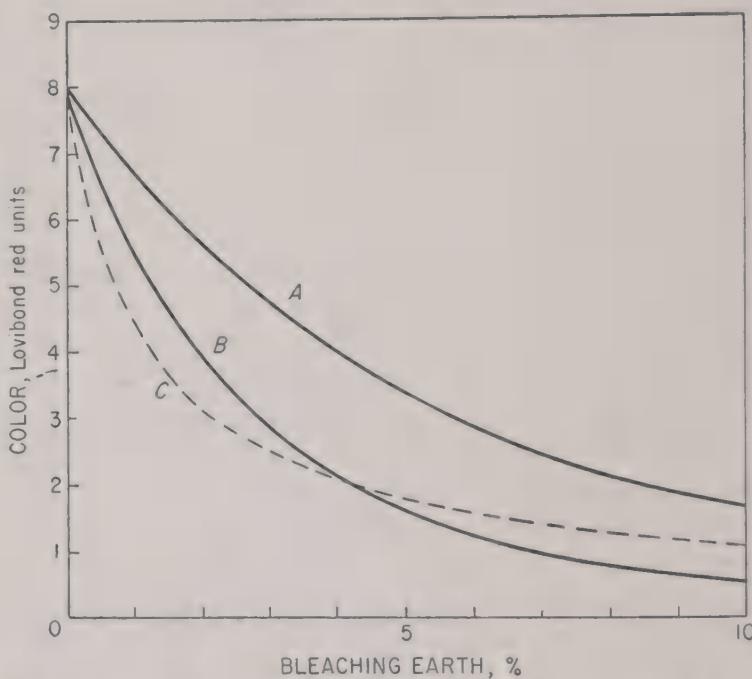
Fig. 96. Theoretical bleaching curves for different values of K and n: (A) $K = 0.5$, $n = 0.5$, (B) $K = 1.0$, $n = 0.5$; (C) $K = 0.6$, $n = 1.2$.

of oxidative stabilization of pigments is supported by experiments which demonstrated that oils bleached much better under vacuum than when exposed to the atmosphere even when they were characteristically "non-reverting" in color, i.e., when mild oxidation of the oil alone brings about a reduction rather than an increase in the color. Obviously, in the presence of oxygen color changes are complex. Simultaneously, there may be darkening of existing pigments, development of pigments from colorless

[80] C. J. Robertson, R. T. Munsberg, and A. R. Gudheim, *Oil & Soap*, *16*, 153–157 (1939).
[81] R. R. King and F. W. Wharton, *J. Am. Oil Chem. Soc.*, *26*, 201–207 (1949).

precursors, destruction of other pigments, modification of pigments to reduce their adsorbability, and adsorption of the different pigments and pigment products to different degrees.

Ordinarily, bleaching has little effect on the acidity of oils. Neutral or slightly acid clays often reduce the acidity very slightly, through preferential adsorption of the free fatty acids. On the other hand, acid clays may increase the acidity measurably (several hundredths of one per cent), especially if moisture or soap are present, or if the contact time with the oil is prolonged. Odeen and Slosson[72] suggest that the clay decomposes soap, adsorbing the sodium ion and leaving the fatty acid free. In treating soapy oils they recommend heating the batch to 220°F., allowing it to stand for an hour or two, and then skimming off the surface layer of separated soap, before proceeding with the bleaching operation.

Mitchell and Kraybill[82] have demonstrated by means of ultraviolet absorption spectra that commercial bleaching commonly produces 0.1–0.2% of conjugated fatty acids in the glycerides of cottonseed, corn, soybean, and linseed oils, through the isomerization of nonconjugated fatty acids. Their observation is of some interest in its relation to the stability of bleached oils, in view of the readiness with which oxidation occurs in conjugated acids, and the autocatalytic nature of the oxidation reaction in fats. Since some degree of prior oxidation was found to be prerequisite to this isomerization, it would seem that it might be maintained at a minimum by deaerating the oil before bleaching, and carrying out the bleaching under a vacuum. Continuous vacuum bleaching should be particularly effective in inhibiting isomerization, since the latter presumably requires appreciable time, and the time of contact between earth and oil is much shorter in continuous bleaching than in bleaching by the batch system. Recently, in comparing plant results with continuous vacuum bleaching vs. open-kettle batch bleaching, King and Wharton[83] have reported significantly better flavor stability in soybean oil processed by the former method.

In addition to decolorizing, treatment of an alkali-refined oil with bleaching earth serves the important function of largely removing traces of soap. The efficiency of soap removal during bleaching appears to depend upon the thoroughness with which the oil and earth are dehydrated during the operation, as the oil retains soap tenaciously only in the presence of dissolved moisture. Because of this, a low soap content is favored by vacuum bleaching, and particularly by continuous vacuum bleaching, where moisture removal is facilitated by spraying the oil and clay slurry into an evacuated chamber. In a series of comparative plant tests King and Wharton[83] found that batch atmospheric bleaching reduced the

[82] J. H. Mitchell and H. R. Kraybill, *J. Am. Chem. Soc.*, *64*, 988–994 (1942).
[83] R. R. King and F. W. Wharton, *J. Am. Oil Chem. Soc.*, *26*, 389–392 (1949).

soap in refined oil from an average of 103 to 32 parts per million, whereas continuous vacuum bleaching effected an average reduction of from 114 to 15 parts per million. The presence of some moisture seems to be essential for good bleaching action. All bleaching earths contain a substantial amount of bound moisture, which is released only at somewhat elevated temperatures. Bleaching earths which have been completely dehydrated by heating to a high temperature are inactive. The presence of moisture in the oil at the beginning of the bleaching operation has no adverse effect.

In general, there is no highly critical temperature for optimum bleaching results, and in most plants bleaching is carried out uniformly at a temperature in the neighborhood of 220–240°F. However, some activated earths yield slightly better results at a lower temperature; hence if the operation is carried out under vacuum, so that dehydration of the oil and earth constitutes no problem, temperatures as low as 170–180°F. are recommended. In a study of atmospheric bleaching of cottonseed and soybean oil in the laboratory, Stout and co-workers[84] found that optimum temperatures for the removal of *yellow* color (475 mμ) varied from 212° to 223°F. for different activated earths and activated carbon, and from 221° to 270°F. for different natural earths. A temperature not in excess of 170°F. is recommended for the bleaching of red oil (commercial oleic acid) with activated earth. On the other hand, temperatures in the range of 300–350°F. are usually used in bleaching palm oil, because of the instability of carotene to heat. Magnesium silicate adsorbents, which are occasionally used for bleaching fatty oils, require much higher temperatures than ordinary bleaching earths (*ca.* 400°F.) for optimum effect.

Bleaching adsorbents come to an equilibrium with the pigments in oils quite rapidly with reasonably efficient stirring of the slurry; for all practical purposes, a contact time of 10–15 minutes may be considered ample. Pigments are adsorbed irreversibly; in fact, they are not removed to any large extent even when the spent adsorbent is extracted with a nonpolar solvent such as petroleum naphtha, although they may be removed with a polar solvent such as acetone. In commercial operation, the spent absorbent in the form of a cake in the filter press, is usually blown for a prolonged period with air and steam, to recover as much as possible of the entrained oil. The recovered oil or "press steamings" is a dark-colored, partially oxidized product, which cannot be incorporated in the bleached oil, but must be re-refined.

(c) Batch Bleaching

The oldest method of bleaching, which is still followed in many plants, involves the use of open cylindrical cone-bottom kettles with mechanical

[84] L. E. Stout, D. F. Chamberlain, and J. M. McKelvey, *J. Am. Oil Chem. Soc.*, **26**, 120–126 (1949).

agitators and steam heating coils. Such kettles are preferably not larger than about 60,000 pounds in capacity, as it is desirable to complete the separation of earth from the oil reasonably soon after the earth is added. The agitator should be designed to maintain the earth in suspension and provide efficient stirring without splashing or aeration at the surface. Heating should be as rapid as possible, and the total heating period should never exceed about one hour.

Most operators add the bleaching earth or mixture of earth and carbon to the kettle in the desired amount somewhat before the top bleaching temperature of about 220–230°F. is reached, e.g., at 160–180°F. Often the earth is mixed in a concentrated slurry with a portion of the oil in a separate small tank which is placed in a dustproof room or provided with dust-collecting equipment. After heating is completed, agitation is continued for 15–20 minutes, and pumping of the oil through the filter press is started. The first oil through the press is returned to the kettle, for clarification, and to build up a press cake and attain a maximum "press bleaching effect." After a minimum color is achieved in the re-circulating oil, the latter is diverted to bleached oil holding or storage tanks.

The cake of spent earth in the filter press is blown with air and steam to recover as much as possible of the entrained oil. Blowing practices vary in different plants. A common procedure is to blow lightly with air for a few minutes, until most of the free oil in the press chambers is dis-placed, then blow with dry steam for 30–45 minutes at about 15–45 pounds pressure, and finally, blow with air for about 15 minutes at about 45 pounds pressure. It is preferable to use presses which have a discharge into a closed line, to avoid blowing a fog of oil particles into the press room. The blow line goes into a small closed tank vented to the outside atmosphere; from this tank condensed water is drawn off and the re-covered oil is pumped back to the refining plant for reprocessing. When an acid-activated earth is used, the press should be cleaned immediately after blowing, to avoid acid injury to the cotton press cloths.

Because of the greater protection afforded the oil against oxidation, batch bleaching is usually conducted under vacuum in the more modern plants. A common vacuum bleaching vessel has a capacity of about 30,200 pounds. It is cylindrical in form, with dished bottom and cover, equipped with a motor-driven agitator and heating and cooling coils. The agitator, unlike that for open kettles, should be designed to roll the charge and constantly bring fresh material to the surface, to assist in deaeration. To provide a larger surface and more splashing at the surface, European processors frequently use horizontal cylindrical vessels, though they are uncommon in this country. The oil inlet should be designed to splash the oil into the evacuated vessel as the latter is charged. A two-stage steam

ejector capable of maintaining a vacuum of **27–28.5** inches is used for evacuation.

Operation of the batch vacuum bleacher does not differ greatly from that of the open bleaching kettle. Some operators add the adsorbent at the beginning of the heating period; others prefer to have the oil at bleaching temperature (usually **220–230° F.**) before it is added, as thereby dehydration of the charge is facilitated. The earth may be pulled from a hopper into the vessel by vacuum through a 3–4 inch line, as it will flow almost like a liquid. After the usual 15–20 minute period of agitation, the batch is cooled to 160–180° F. and filtered as described above.

(d) Continuous Bleaching

Continuous vacuum bleaching protects the oil from the harmful effects of oxidation even more effectively than batch vacuum bleaching, since
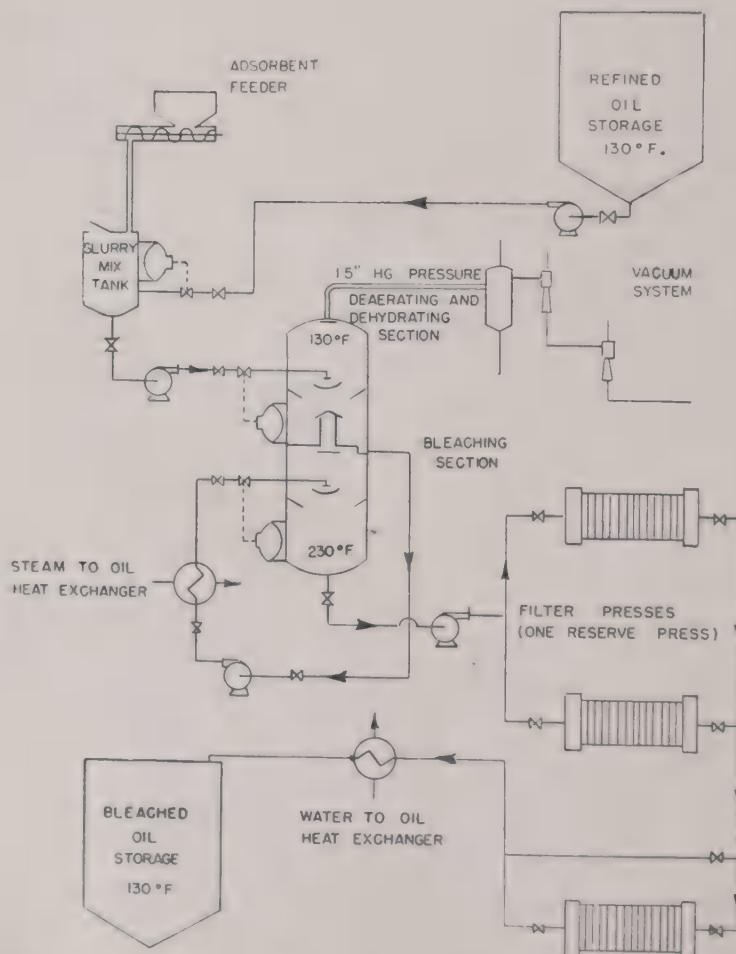
Fig. 97. Flow diagram, continuous vacuum bleaching process, according to King *et al.*[20]

better deaeration is effected by spraying the oil into a vacuum than can ordinarily be obtained by agitating a large batch under vacuum. Also the oil and earth are more completely deaerated, and the contact time between oil and earth is reduced. This reduces the soap content of the bleached oil, minimizes free fatty acids development when acid earths are used, and has been reported to produce oil of improved flavor stability.[83] Economy in earth usage and oil retention is achieved by avoiding oxidation and, in one process, by filtering the feed oil through partially spent earth, to achieve two-stage countercurrent operation. By effecting heat exchange between the feed and the bleachd oil some saving of heat is possible.

The continuous vacuum bleaching process of King et al.[83,85] is illustrated in Figure 97. Feed oil from storage is mixed continuously with adsorbent in metered amount, and the resulting slurry is sprayed into the top section of an evacuated tower, to flash off dissolved air and free moisture. It is then withdrawn from the tower, heated to bleaching temperature, and resprayed into a second bottom section of the tower, to remove bound moisture which is released from the earth only after it is heated. A small amount of stripping steam in each section provides agitation and assists in the removal of moisture and air. From the second section the oil–clay mixture is pumped through closed filter presses to remove the clay, and thence through a cooler to storage.

A somewhat similar continuous bleaching process, which omits the second spraying effect, has been patented by Robinson.[86]

The continuous bleaching process described above has been modified[87] to provide the advantages of flash deaeration and drying and at the same time give the effect of two-stage countercurrent flow between earth and oil. The apparatus, illustrated in Figure 98, is similar to that used by King et al., except that the clay feeder and mixing tank are not open to the atmosphere, but are maintained under vacuum. The cold feed oil is sprayed into the vacuum tower to remove dissolved air and moisture, pumped from the tower through a heat exchanger and a heater, to raise it to bleaching temperature, then through a filter press containing partially spent clay, where a portion of the color is removed, and finally to the evacuated mixing tank where fresh earth is metered and mixed into it. From the mixer, the slurry goes back into another section of the tower for moisture removal, then into a closed filter press, where the earth is removed. The filtered oil passes through a heat exchanger, where it exchanges heat with the cold oil from the tower, and then through a cooler to storage. Three filter presses are provided, of which two are always in

[85] R. R. King, S. E. Pack, and F. W. Wharton (to Mrs. Tucker's Foods, Inc.), U. S. Pat. 2,428,082 (1947).
[86] A. A. Robinson (to Standard Brands, Inc.), U. S. Pat. 2,483,710 (1949).
[87] See A. R. Baldwin, J. Am. Oil Chem. Soc., 26, 610–614 (1949).
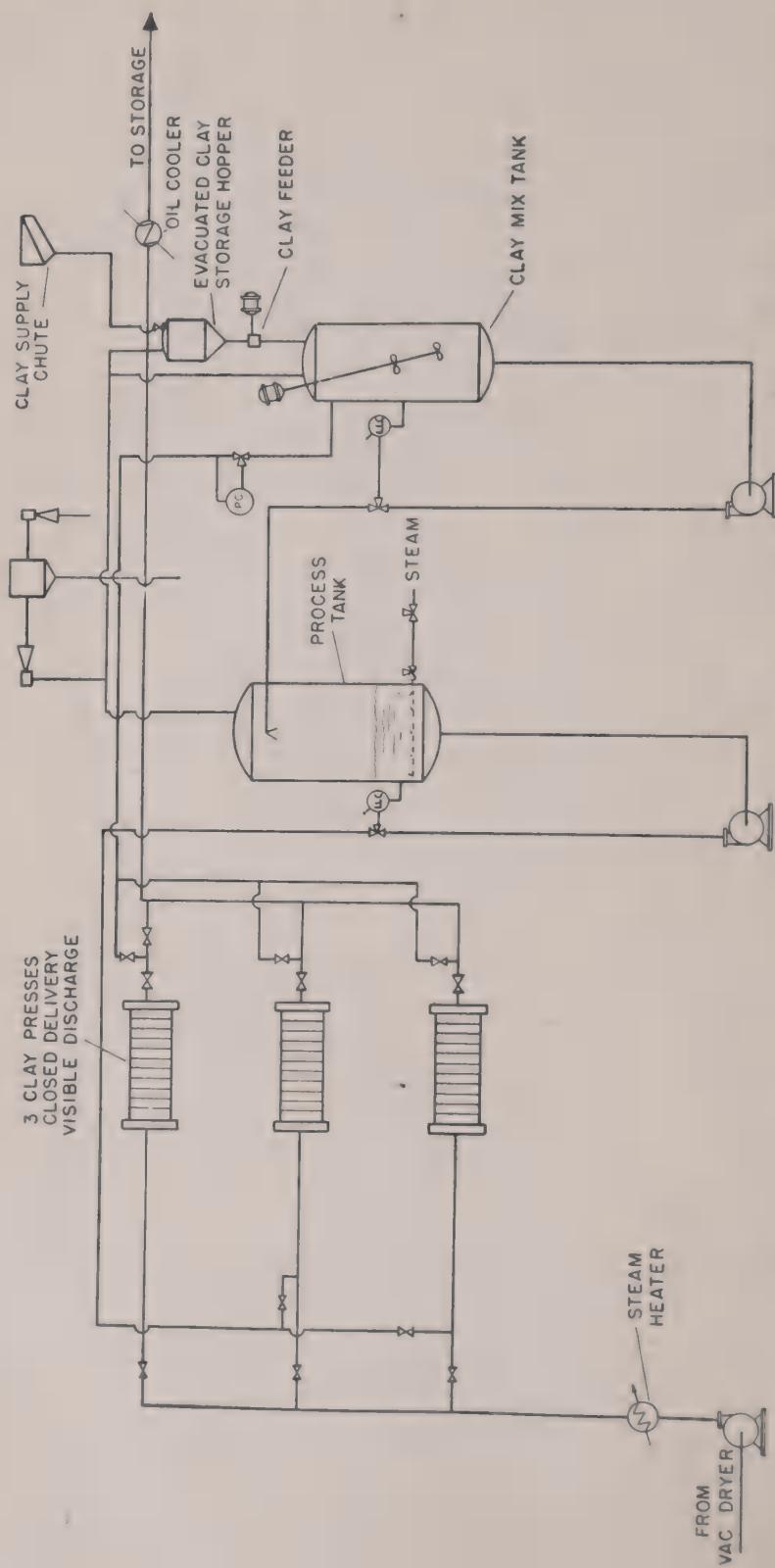
Fig. 98. Flow diagram, continuous two-stage countercurrent bleaching system. (Courtesy *The Girdler Corp.*).

operation while the third is out of service for cleaning. The presses are so manifolded that the flow of oil can go through any two of the three in any desired succession. Each time that a press becomes filled with earth accumulated from the clay introduced at the mixing tank, the flow is switched so that the filled press becomes the first in the series, receiving the hot unbleached feed oil, and the empty press just cleaned receives the oil–clay slurry. The press formerly first in the line of flow then becomes idle, so that it may be cleaned.

If the feed oil is taken, not from an open storage tank, but directly from the vacuum dryer of a continuous refining plant, the apparatus can be simplified by omission of the first spraying or deaerating operation, with the feed going directy through heaters to the first filter press.

The countercurrent feature of the above process leads to some economy of earth usage; as mentioned previously, this depends upon the fact that earth in equilibrium with the finished bleached oil still has some capacity for removing color from the darker feed oil as the latter passes through the first press.

(e) Recovery of Oil from Spent Bleaching Earth

Because of the inexpensiveness of the equipment required (an open tank with steam coils), a process of "boiling off" is used more than any other for the recovery of oil from spent bleaching earth. Details of the method vary, but in all cases it involves prolonged boiling of the earth with a weakly alkaline aqueous solution to displace the oil from the earth without saponifying any considerable amount of neutral oil, and salting out the resulting emulsion to separate an oil layer. Recovery of the oil is incomplete, but it is possible to reduce the oil content of the earth from 30–40% to about 6–8%.

An autoclave method of deoiling described by Werth[88] is claimed to be capable of reducing the oil in spent earth to 2–3%. The autoclave, which must be capable of withstanding a pressure of about 3 atmospheres (275°F.) and provided with a mechanical agitator, is charged with 400 kg. (880 lbs.) of earth, 400 l. (106 gals.) of water, 12 kg. (26.5 lbs.) of calcined soda or its equivalent in the form of sodium hydroxide, and 12 kg. (26.5 lbs.) of salt. With the agitator running, the earth is gradually added to the aqueous solution of the alkali and salt, the autoclave is closed, steam is admitted, and the treatment is continued for several hours with agitation. Stirring is then discontinued, the autoclave is blown down, and after a settling period of several hours, an upper layer of oil is drawn off, a lower layer of sludge is discharged, and an intermediate emulsion layer

[88] A. van der Werth, in Hefter-Schönfeld, *Chemie und Technologie der Fette und Fettprodukte.* Vol. II, Springer, Vienna, 1937, pp. 66–68.

is taken off to an oil separator, for further settling. The recovered oil is stirred with a small amount of sulfuric acid, to deposit sediment, settled, and washed with water.

Somewhat more efficient recovery of the oil may be obtained by extraction of the earth with petroleum naphtha or other nonpolar solvent; polar solvents are undesirable because of the large amount of pigments and oxidized and polymerized oil that they remove from the earth. A solvent extraction plant which has been in commercial operation in this country for a number of years has been described by Sieck.[89] Other, more modern plants are also in operation, but details of their design or operation are not publicly available.

Although the oil recovered from bleaching adsorbents is usually dark-colored and of poor quality, because of oxidation which occurs during blowing of the press cake, it appears that it should be possible to recover an oil of high grade by avoiding prolonged press blowing and depending purely upon extraction for efficient oil recovery. Solvent extraction should be particularly applicable to the press cake from continuous bleaching systems.

As mentioned previously, the spent earth is discarded at many refineries without any attempt at oil recovery.

3. CHEMICAL BLEACHING

Some of the carotenoid pigments and possibly other coloring matters in fats and oils are converted to colorless or nearly colorless materials by oxidation. Consequently, bleaching by oxidation constitutes one of the available methods for producing light-colored oils. Obviously it is impossible to oxidize the pigments in an oil without likewise oxidizing the glycerides of the oil to some extent, as well as destroying natural antioxidants. For this reason, bleaching by oxidation is of limited applicability. It is never employed in the treatment of edible fats, and its chief usefulness is in bleaching palm oil or dark-colored animal fats for soapmaking.

In some cases oils are bleached by means of atmospheric oxygen, the batch being simply blown with air for several hours at a moderately elevated temperature, e.g., 150–200°F. Bleaching by aeration is particularly effective in the case of palm oil, since carotene is readily bleached by oxidation, and this oil is sufficiently low in iodine value for it to be possible to oxidize the pigments without oxidizing the oil itself to any advanced degree.

Most of the chemical agents which have been employed for bleaching are oxidizing agents. Among these, sodium dichromate is one of the more common, being often used by soapmakers for bleaching palm oil. The

⁸⁹ H. Sieck, *Oil & Soap*, *14*, 314–315 (1937).

chrome bleaching of palm oil is described by Thomssen and Kemp[90] as follows: If the oil contains an appreciable amount of settlings or solid material, these are first removed by boiling the charge with a 10% salt solution and wet steam, and allowing it to settle. Bleaching is conducted in a lead-lined tank, equipped with perforated coils for the injection of both steam and air. The charge consists of one ton of oil. The oil is brought to a temperature of 110°F., and 40 pounds of fine dry salt are sprinkled into the tank. Then there are added 40 pounds of concentrated commercial hydrochloric acid, and 17 pounds of sodium dichromate dissolved in 45 pounds of the same acid. The latter solution is added slowly, over a period of about three hours; the charge is agitated with air during the addition of the dichromate solution, and for one hour thereafter. At the end of this time, agitation is stopped and the aqueous phase is allowed to settle to the bottom of the tank, from which it is drawn off. Water to the amount of 40 gallons is then added, and the charge is agitated and heated with open steam to 150–160°F., after which the operation is completed by allowing the contents of the tank to settle overnight.

The bleaching of inedible tallows and greases with chlorine dioxide, generated *in situ* by the action of sulfuric acid on sodium chlorite, has been described by Woodward and co-workers.[91] The fat, at 210°F., is agitated for 0.5–1.0 hour with 0.1% sodium chlorite and sufficient sulfuric acid to lower the pH to 4 or below, after which the pH is raised to 8 by the addition of 8° Bé. caustic soda solution, the watery layer is drawn off, and the fat is dried. The corrosive effects of acid on the equipment can be avoided by using gaseous chlorine to liberate the chlorine dioxide, or by using dry chlorine dioxide as such.

[90] E. G. Thomssen and C. R. Kemp, *Modern Soap Making.* MacNair-Dorland Co., New York, 1937, pp. 30–32.

[91] J. B. Tuttle and E. R. Woodward. *Chem. & Met. Eng.*, *53*, No. 5, 114–115 (1946); E. R. Woodward and G. P. Vincent. *Soap Sanit. Chemicals*, *22*, No. 9, 40–43, 137, 139, 141 (1946).

HYDROGENATION[1]

A. Introduction

1. Nature of the Process

Hydrogenation of a fat consists in the direct addition of hydrogen at double bonds in the fatty acid chains, according to the following scheme:

$$
\begin{array}{ccc}
\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}=\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C} }& +\ H_2\ = & \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}
\end{array}
$$
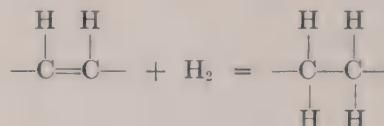
Thus, the degree of hydrogenation in an oil is directly related to the iodine value, the addition of one mol of hydrogen corresponding to the absorption of one mol of iodine. It can be calculated, therefore, that 0.0795 pound of hydrogen is required to reduce the iodine value of 1000 pounds of oil 1 unit. This amount of hydrogen corresponds to 14.15 cubic feet of hydrogen measured at 0°C. and 760 mm. pressure, or 14.95 SCF or cubic feet measured, according to standard commercial practice, at 60°F. and 14.70 pounds per square inch absolute pressure.

Since oils are seldom hydrogenated to produce a reduction in iodine value of more than about 120 units, the weight of the oil is usually increased less than 1%.

Primarily, hydrogenation is a means of converting liquid oils to semi-solid, plastic fats, suitable for shortening or margarine manufacture. However, it also accomplishes various other desirable purposes, includ-

[1] General References: H. Adkins, *Reactions of Hydrogen with Organic Compounds Over Copper-Chromium Oxide and Nickel Catalysts*, Univ. of Wisconsin Press, Madison, 1937. S. Berkman, J. C. Morrell, and G. Egloff, *Catalysis*, Reinhold, New York, 1940. J. W. Bodman, E. M. James, and S. J. Rini, Chapter XVII, in *Soybeans and Soybean Products*, K. S. Markley, ed., Interscience, New York, 1950. C. Ellis, *Hydrogenation of Organic Substances*, 3rd ed., Van Nostrand, New York, 1930. E. Hugel, in H. Schönfeld, ed., *Chemie und Technologie der Fette und Fettprodukte*, Vol. II, Springer, Vienna, 1937, pp. 135–214. T. P. Hilditch and C. C. Hall, *Catalytic Processes in Applied Chemistry*, 2nd ed., Van Nostrand, New York, 1937. H. W. Lohse, *Catalytic Chemistry*, Chemical Pub. Co., Brooklyn, 1945. J. W. McCutcheon, *Can. Chem. Process Inds.*, 33, 53–57 (1939). Natl. Research Council, *Twelfth Report of the Committee on Contact Catalysis*, Wiley, New York, 1940. P. Sabatier, *Catalysis in Organic Chemistry*, translated by E. E. Reid, Van Nostrand, New York, 1922. H. S. Taylor, *Industrial Hydrogen*, Chemical Catalog Co. (Reinhold), New York, 1921.

ing enhancement of the stability and improvement of the color of the fat.

The reaction requires a catalyst; the catalyst employed in commercial hydrogenation invariably consists basically of nickel, although minor amounts of copper, alumina, etc., may be incorporated with the nickel for their "promoter" action. There has been some use of massive catalysts for continuous hydrogenation, but by far the greatest amount of hydrogenation is carried out with powder catalysts composed of the metal or metals in a finely divided form, prepared by special methods, and often supported on a highly porous, inert, refractory material, such as kieselguhr. The catalyst is suspended in the oil during the operation of hydrogenation, and at the conclusion is removed by filtration. Although catalysts decrease in activity with repeated use, in most cases inactivation is slow, and a single charge of catalyst is ordinarily used a number of times.

For hydrogenation to take place, it is necessary to bring together at a suitable temperature, gaseous hydrogen, liquid oil, and the solid catalyst. In ordinary practice it may be assumed that the hydrogen is first caused to dissolve in the oil, and the hydrogen-laden oil is then brought into contact with the catalyst by mechanical means. In the usual type of equipment, reaction is brought about by agitating the suspension of catalyst and oil in a closed vessel in an atmosphere of hydrogen. Agitation of the catalyst–oil mixture serves the double purpose of promoting solution of hydrogen in the oil, and continuously renewing the oil at the catalyst surface. The solubility of hydrogen and other gases in oil, unlike their solubility in water, increases with increasing temperature, and of course is also increased by pressure.

The rate at which hydrogenation will proceed under the conditions outlined above depends upon the temperature, the nature of the oil, the activity of the catalyst, the concentration of the catalyst, and the rate at which hydrogen and unsaturated oil molecules are supplied together to the active catalyst surface. The composition and character of the hydrogenated product may vary according to the positions of the double bonds which are hydrogenated, as well as certain isomerizing influences accompanying the reaction, and are highly dependent upon the conditions of hydrogenation.

Although in the foregoing, mention has been made only of the hydrogenation of glycerides, the process is equally applicable to fatty acids, to nonglyceride esters, or to other unsaturated fatty acid derivatives.

2. Historical

The modern hydrogenation process had its origin in the classical research of Sabatier and Senderens,[2] carried out within the period *ca.* 1897–

[2] See reference to P. Sabatier, footnote 1.

1905, which demonstrated the feasibility of effecting hydrogenation of unsaturated organic materials in simple apparatus and without an undue occurrence of side reactions, using nickel or other relatively cheap metal as a catalyst.

Actually, Sabatier's experiments encompassed hydrogenation in the vapor phase only; hence his technique was not directly applicable to relatively nonvolatile triglycerides. A process for the liquid phase hydrogenation of fatty oils was patented by Normann[3] in 1903. Title to the Normann patent passed to the British firm of Joseph Crossfield & Sons. and hydrogenation is said to have been employed on a limited scale in the treatment of whale oil in England in 1906 or earlier.[4] Potentially, however, the greatest use for the process lay in the United States, where a vast production of cottonseed oil awaited technical developments which would permit its conversion to the plastic edible fat demanded by American tradition and custom.

In 1909 the American rights to the Crossfield patents were acquired by the Procter & Gamble Company, which placed its hydrogenated cottonseed oil shortening, Crisco, on the market in 1911. Promotion and marketing of the new product was prosecuted with vigor and with sufficient success to arouse the strong interest of other American processors. Later, a court decision invalidated the Burchenal patent,[5] under whose broad claims the Procter & Gamble shortening was then manufactured, and the way was cleared for the manufacture of comparable products by other firms. At the present time hydrogenation is employed by virtually every American produced of shortening or margarine oils and by most margarine manufacturers elsewhere in the world. as well as by many processors of nonedible oils and fats.

3. Importance of Hydrogenation

It is difficult to exaggerate the importance of the hydrogenation process in modern oil and fat technology. It is employed on a vast scale in both the soap and edible fat industries, for converting liquid oils to hard or plastic fats, for converting soft fats to firmer products, and for improving the resistance of fats and oils to deterioration through oxidation or flavor reversion. To a far greater extent than any other process it has contributed to the present high degree of interchangeability among a wide variety of fats and oils. The most obvious result of the introduction of hydrogenation on a wide scale has been the establishment of liquid oils, such as cottonseed and other vegetable seed oils, and marine oils, as adequate sub-

[3] W. Normann, Brit. Pat. 1,515 (1903).
[4] G. M. Weber and C. L. Alsberg, *The American Vegetable Shortening Industry*. Food Research Institute. Stanford University. 1934.
[5] J. J. Burchenal, U. S. Pat. 1,135,351 (1915).

stitutes for originally more expensive hog and beef fats. It is a mistake, however, to think of hydrogenation merely as a means of producing substitute products, inasmuch as hydrogenated fats may be superior in important respects to any of the natural plastic fats. In many instances, too, hydrogenation is now being employed to improve the consistency or stability of animal fats, as in the hydrogenation of lard or lard stearine, the hydrogenation of oleo oil for margarine manufacture, the hydrogenation of greases for soapmaking, etc.

B. Theory of Catalysis

1. General Considerations

(a) *Definition of a Catalyst*

A catalyst, according to the classical definition of Ostwald, is a substance which alters the rate of a chemical reaction, without affecting the energy factors of the reaction or being consumed in the reaction. Properly speaking, therefore, a catalyst cannot initiate but can only accelerate a reaction. However, in numerous instances, of which the hydrogenation of fats and oils is an example, reaction is so imperceptibly slow in the absence of a catalyst that the latter may for all practical purposes be considered an essential element of the reacting system.

The permanent or self-regenerative nature of catalysts is very important. Although in the course of their action catalysts may enter into temporary combination with the reactants, such combinations are unstable and invariably are broken down at the completion of the reaction, to yield the catalyst is an unchanged form. Thus the catalyst enters into the reaction over and over again, and a relatively small amount may be capable of transforming very large amounts of material. Ordinarily, the concentration of nickel employed as a catalyst for the hydrogenation of fats does not exceed a few hundredths of one per cent of the weight of the fat.

The fact that a catalyst cannot initiate reactions does not mean that the introduction of a catalyst into a reacting system may not influence the composition of the reaction products, or that different catalysts may not yield different products. In many cases, reaction may follow a number of alternative courses; hence the composition of the final products will depend upon the relative rates of the various alternative reactions. Where a number of different reactions occur together, the addition of a catalyst to the system may accelerate certain of these to a far greater extent than others. Furthermore, one catalyst may differ from another in its relative effect on the different reaction rates. The hydrogenation of fats and oils furnishes examples of such specificity of catalyst action. Thus the addi-

tion of hydrogen to a linoleic acid chain in a glyceride molecule may yield either normal oleic acid or isomeric forms of this acid. Some nickel catalysts are much more inclined than others to produce the isomeric forms.

(b) *Heterogeneous Catalysis*

The type of catalysis which is the most important in industry, and the type which is operative in fat hydrogenation, is heterogeneous catalysis. By definition, a heterogeneous system is one in which the catalyst and the reactants exist in different physical states. Actually, such systems are in practice confined to those in which the catalyst is a solid and the reactants are liquids or gases. Heterogeneous catalysis is to be somewhat sharply distinguished from homogeneous catalysis, in which the catalyst and the reactants comprise a single phase. In homogeneous catalysis the catalyst functions in the form of individual molecules, which are uniformly distributed throughout the reacting system. Thus the question of catalyst structure, or of surface phenomena, does not enter. On the other hand, in heterogeneous catalysis it is the catalyst surface which performs the catalytic function; hence the nature of the surface is of extreme importance. A catalyst operating in a homogeneous system is defined simply in terms of its chemical constitution and its concentration in the system. With all other factors controlled, the effect of a homogeneous catalyst of definite composition is exactly predictable upon the basis of its concentration. However, if the catalyst is a solid, its behavior will depend not only upon its chemical composition, but also to a very large degree upon both the nature and extent of its surface. The fact that the characteristics of a solid catalyst are determined so largely by the submicroscopic character of its surface renders the study and control of such catalysts very difficult. Apparently similar catalysts may differ enormously in their activity and considerably in their specific action.

In heterogeneous catalysis it is now generally assumed that reaction proceeds through the formation of unstable intermediate compounds or adsorption complexes, in which the catalyst is temporarily combined with one or more of the reactants. If such compounds exist, it is probable that in most cases they are not definite chemical combinations, but consist merely of strongly bound molecules of the reactant which are held to the catalyst surface by secondary valence forces. In any event, it is essential that they be unstable, *i.e.*, capable of being either decomposed or desorbed, to permit reaction to proceed according to the following scheme:

$$\text{Catalyst + reactants} \xrightarrow{\text{adsorption}} \text{catalyst-reactant complex}$$

$$\xrightarrow{\text{desorption}} \text{reaction products + regenerated catalyst}$$
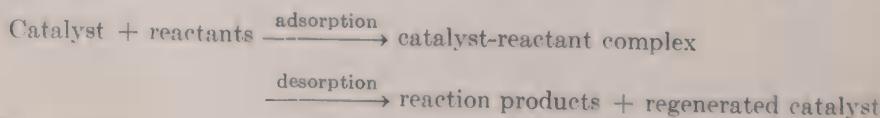
(c) *Catalysis in Relation to Energy of Activation*

Chemical reactions, catalyzed or uncatalyzed, proceed at relatively slow rates and do not occur instantaneously principally because of a pattern of molecular distribution of energy which insures that at any instant but a few molecules of the reacting substances will be at a high energy level. The critical energy for a specific reaction, known as the energy of activation, may be represented graphically as the height of a potential barrier opposing the reaction (Fig. 99).
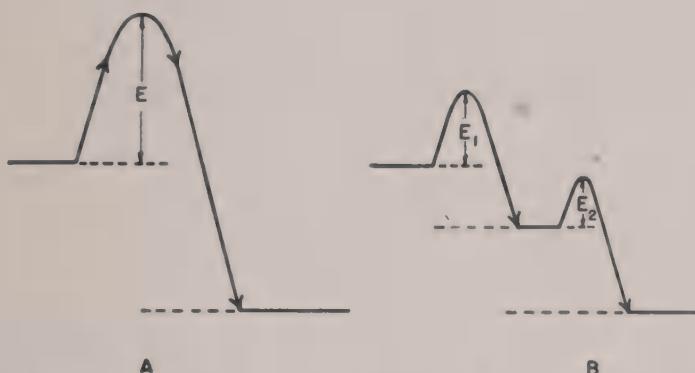
Fig. 99.   Graphical representation of the activation energy factor in: (*A*) uncatalyzed and (*B*) catalyzed reactions (after Grosse[7]).

Modern views relative to the energy factor in catalysis have been reviewed by Berkman, Morrell, and Egloff.[6]   More recently, Grosse[7] has presented a simplified treatment of catalytic action from the standpoint of energy relationships, from which the following is taken.

The rate of a chemical reaction, k, is determined by the integrated Arrhenius equation:

$$k = ae^{-E_{act.}/RT}$$

where T is the absolute temperature, a is a factor related to the concentration of the reactants, and $E_{act.}$ represents the activation energy. Due to the exponential character of the above equation, a relatively slight change in activation energy will have a large effect on the reaction rate. Thus, for example, it is calculated that if the activation energy at 300°K. is 50,000 calories, a 10% lowering of this energy requirement will increase the reaction rate 4400 times, whereas even a 1% lowering will increase it 2.3 times.

Catalysts increase the reaction rate through their influence on the ac-

[6] See reference to Berkman *et al.* in footnote 1.
[7] A. V. Grosse, *Ind. Eng. Chem., 35,* 762–767 (1943).

tivation energy. A catalyst breaks the reaction up into two steps, which are successively the combination of catalyst and reactants to form an unstable intermediate compound, and the breakdown of this compound, to yield a new product and the free catalyst. This has the effect of permitting the aforementioned barrier to be surmounted in two small steps, rather than one large one (Fig. 99). Or in other words, two reactions with relatively low activation energies are substituted for a single reaction with a high activation energy. The alteration thus caused in the reaction rate is measured by the difference between the activation energy of the uncatalyzed reaction and that of the slower of the two steps of the catalyzed reaction. In view of the exponential relation outlined above, it is readily apparent that the catalyzed reaction may proceed at a rate which very greatly exceeds that of the uncatalyzed reaction.

2. Catalysis in Hydrogenation of Fats

Present opinion appears to be in general accord with the postulate originally set forth by Armstrong and Hilditch[8]—that fat hydrogenation involves the formation of a hydrogen–nickel–unsaturated fatty acid radical complex, which breaks down to yield a fatty acid radical of increased saturation, plus the free nickel catalyst.

This being so, the hydrogenation behavior of any particular substance may be expected to depend to a considerable degree upon its surface activity with respect to the catalyst, i.e., upon how strongly it tends to be adsorbed by the catalyst surface.

In general, different fatty materials appear to be held to the catalyst surface as to the surface of any other adsorbent, for example, the adsorbents used for chromatographic separations: free acids are held more strongly than corresponding esters, and hence tend to hydrogenate selectively in mixtures of the two (see page 710); saturated fatty acid radicals have little affinity for the catalyst; and unsaturated radicals have a progressively greater affinity as their unsaturation increases, with a particularly strong attraction existing where there is an active methylene (CH_2) group between two double bonds.

In the past, it has been generally assumed that a single collision of an unsaturated fatty acid radical with hydrogen and active nickel is sufficient to hydrogenate but one double bond. In other words, hydrogenation is assumed to occur stepwise in the case of a polyunsaturated fatty acid radical, e.g., linolenic → linoleic → oleic → stearic, with breakdown of the above-mentioned complex and desorption of the fatty acid occurring at the end of each step. This is probably the case in the sequence, linoleic → oleic → stearic; or in any analogous progression from two isolated

[8] E. F. Armstrong and T. P. Hilditch, *Proc. Roy. Soc. London*, A98, 27–40 (1920).

double bonds, to one, to none. There is evidence, however, that the hydrogenation of linolenic fatty acid radicals may proceed in part directly to the formation of oleic acid, without intermediate desorption of linoleic acid from the catalyst.[9,10] Evidently, two of the three double bonds in triethenoid conjugated fatty acid radicals also hydrogenate simultaneously.[11,12]

C. General Characteristics of the Reaction

1. Mechanism of Bringing Together Reactants

As indicated previously, hydrogenation of fatty materials can take place only after there has been brought about a conjunction of three different reactants: hydrogen, an unsaturated fatty acid radical, and the active portion of a metallic catalyst. Since the three consist, respectively, of gas, liquid, and solid, the mechanism whereby conjunction is achieved is somewhat involved. However, many of the characteristics of the hydrogenation reaction are not intelligible without careful consideration of the nature of this mechanism.

It has been mentioned above that the catalyst has a definite affinity or adsorptive power for both hydrogen and unsaturated fatty materials. Whether hydrogen is first adsorbed by the catalyst, which then adsorbs, reacts with, and then desorbs the fatty molecule—or adsorption of the fat occurs first—or adsorption of either occurs indifferently—is not at present known. It is certain, however, that the concentrations of hydrogen, of unsaturated molecules, and of catalyst have each an influence on the rate at which hydrogenation proceeds. Furthermore, in special cases any one of the three may become so small in relation to the other two as effectively to control the reaction rate.

In practice, the concentration of catalyst is, of course, constant and known; and the concentration of unsaturated fat molecules may be determined at any time by simple analytical methods. The concentration of hydrogen may not be so determined, however, but may be only inferred—and inferred very uncertainly—from such factors as the pressure on the system and the thoroughness with which hydrogen is mixed into the oil. It should be particularly pointed out that it is the concentration of hydrogen *dissolved in the oil* and not the concentration of hydrogen in the gas phase that must be considered in relation to the kinetics of the reaction. Failure to appreciate this fact has in the past caused much confusion among writers and workers in the field.

[9] A. E. Bailey and G. S. Fisher, *Oil & Soap*, *23*, 14–18 (1946).
[10] A. E. Bailey, *J. Am. Oil Chem. Soc.*, *26*, 644–648 (1949).
[11] E. H. Farmer and R. A. E. Galley, *J. Chem. Soc.*, *1933*, 687–696.
[12] T. P. Hilditch and S. P. Pathak, *Proc. Roy. Soc.*, *A198*, 323–337 (1949).

The factors of hydrogen pressure and degree of agitation are commonly listed among those determining the rate and character of the reaction. However, insofar as the author is aware, there is no evidence that these factors have any effect except as they influence the concentration of hydrogen in the liquid phase.[13] The manner in which they exert such influence may be appreciated from a consideration of the mechanics of gaseous diffusion.

The equation defining the rate at which a gas may dissolve in a stirred body of liquid has the form:

$$dp_l/dt = kA(p_g - p_l)$$

where dp_l/dt is the rate of solution, A is the magnitude of the interface between gas and liquid, p_g is the pressure (corresponding to concentration) of the hydrogen in the gas phase, p_l is the pressure (or concentration) of the hydrogen in the liquid phase, and k is a constant related to the properties and thickness of the static film of liquid at the interface. The area of the interface, A, is a function of the degree to which the oil is agitated (or to which the hydrogen is dispersed during its passage through the oil), and p_g, the pressure or concentration in the gas phase is, of course, synonymous with the absolute pressure registered in the system.

In hydrogenation practice the concentration of dissolved hydrogen may vary within wide limits. In the case of an oil having a low iodine value and hence a low concentration of unsaturated fatty acids, or in the case of oil containing very little catalyst, if the agitation is reasonably good, the concentration of dissolved hydrogen may obviously approach closely to saturation. On the other hand, if agitation is relatively poor, the unsaturation of the oil relatively high, and the catalyst concentration likewise high, the concentration of dissolved hydrogen can doubtless fall very low. Such a condition is particularly likely to occur when a high concentration of catalyst is employed in laboratory hydrogenation. It may be recognized by failure of the reaction to accelerate when the amount of catalyst is increased, and also by the rate of reaction remaining constant over a wide range of iodine values, rather than continuously decreasing as the degree of unsaturation falls. The hydrogenation rate depends, under these conditions, simply upon the rate at which hydrogen can dissolve in the oil, and hence is independent, within limits, of the concentration of either of the other two reactants.

Under most conditions the concentration of dissolved hydrogen will be intermediate between the two extremes cited above. However, under

[13] The unlikelihood that augmentation in the reaction rate can be the result of pressure *per se* is also apparent from the volume changes accompanying hydrogenation. The molecular volume of unsaturated fatty acids or glycerides is *increased* when they are hydrogenated. It is assumed here that in any case the agitation will be sufficient to maintain the catalyst in uniform suspension in the oil and prevent the development of localized gradients in the unsaturation of the oil.

fixed conditions it will inevitably vary (increase) as the reaction proceeds, owing to progressive diminution in the concentration of double bonds in the unsaturated fat molecules.

The question of hydrogen concentration in the oil is of importance not only with respect to the reaction rate, but also in relation to the course of hydrogenation and the consequent composition of the hydrogenated product. As was implied above, and as will be developed in a latter section, there is evidence that the factors of agitation, pressure, catalyst concentration, and temperature, are interrelated in their influence on the course of hydrogenation, and that the latter is possibly to be interpreted in terms of the concentration of hydrogen adsorbed on the catalyst.

It has been assumed in the foregoing and will be assumed in subsequent discussion that under any practical conditions of agitation with a powder catalyst there is substantial uniformity of composition in the body of oil. In other words, it is taken for granted that no small portions of the oil will become hydrogenated to an undue degree, at the expense of other portions, because of poor circulation of oil past the catalyst surfaces. The fact that such a condition would lead to a nonselective hydrogenation of the more unsaturated fatty acids, whereas reducing the agitation actually serves to increase selectivity, appears to be evidence that this assumption is justified insofar as commercial hydrogenation is concerned.

2. PREFERENTIAL NATURE OF THE PROCESS

Hydrogenation is preferential in the sense that certain fatty acids—or more accurately, fatty acid radicals—hydrogenate more readily than others, with the readiness of hydrogenation increasing, in general, with increase in the unsaturation. However, the degree to which it is preferential is quite variable, according to the conditions of reaction. This—and the circumstance that preferentiality is accompanied by a definite pattern in the formation of isomers of the natural fatty acids—makes the reaction, to some degree, amenable to control, and accounts in considerable part for the complications that are encountered in the technology of the industry. The different factors which have an influence on the degree of preferentiality will be treated in detail in later sections of this chapter.

(a) Definition of the Term "Selectivity" as Applied to the Reaction

In the following pages, repeated reference is made to the "selectivity" of the hydrogenation reaction. The term is used as defined originally by Richardson and co-workers[14]; it refers to the conversion of linoleic acid to oleic acid preferentially to the conversion of oleic acid to stearic acid, or more exactly, in the light of recent work, to the hydrogenation of acid-

[14] A. S. Richardson, C. A. Knuth, and C. H. Milligan, *Ind. Eng. Chem.*, 16. 519–522 (1924).

containing active methylene groups in preference to acids devoid of such groups. It is to be noted that selective hydrogenation, as thus defined, does not refer specifically to hydrogenation conducted in such a manner as to obtain maximum softness in the fat at a specified iodine value, or a minimum melting point, cloud point, congeal point, etc., even though there may be at times a positive correlation between true selectivity and these various properties. It may be further noted that selectivity is relative and never absolute. Under no conditions, for example, is it possible to stop the hydrogenation of oleic acid altogether and cause hydrogen to enter solely into combination with linoleic acid, so long as oleic acid is present. It is only possible to make the hydrogenation of oleic acid very slow in relation to the hydrogenation of linoleic acid. Actually, it is possible in ordinary practice to vary the ratio of reaction rates, linoleic acid : oleic acid, from about 4 : 1 in very nonselective hydrogenation to about 50 : 1 in very selective hydrogenation.[10]

(b) Definition of Term "Selective" as Applied to Catalysts

As will be explained in more detail later, an invariable result of fat hydrogenation is the formation of a certain amount of high-melting "iso-oleic" acids. The amount formed in any case is in direct proportion to the selectivity of the reaction; however, at a given level of selectivity, different catalysts vary with respect to the amount of iso-oleic acids that they produce and, conversely, at a given level of iso-oleic acid formation there are variations in selectivity (as measured by the formation of saturated acids). By present definition, one catalyst is more selective than another when, under comparable conditions, it produces less iso-oleic acids at a given saturated acid level or less saturated acids at a given iso-oleic acid level. In effect, this is equivalent to saying that the more selective catalyst will produce a hydrogenated oil of softer consistency (at 70–75°F.) and lower melting point at any given iodine value, as well as an oil of softer consistency at a given melting point or of lower melting point at a given consistency.

3. REACTION ORDER AND REACTION RATES

(a) Order of the Reaction

The hydrogenation reaction has several peculiarities which render a mathematical analysis of it difficult. Natural oils and fats invariably contain two or more different unsaturated acids, and isomeric forms appear as the reaction proceeds. All of these absorb hydrogen simultaneously, but at different rates. It has been pointed out previously[15] that even if

[15] H. K. Moore, G. A. Richter, and W. B. Van Arsdel, *J. Ind. Eng. Chem.*, 9, 451–462 (1917). J. W. McCutcheon, *Can. Chem. Process Inds.*, 33, 53–57 (1939).

each of the individual reactions were to follow a simple course, complexity could arise from combination of these in the over-all reaction.

It appears to be fairly well established that, with other conditions fixed, the rate of hydrogenation of any unsaturated acid must be proportional to its concentration in the oil.[10]   Yet, actually, other conditions vary. Catalysts undergo progressive inactivation with use, and the concentration of the other reactant—dissolved hydrogen—is not only not constant, but is also impossible to measure.

In view of the above, it is hardly to be expected that any definite order can be assigned to the reaction as a whole. On the other hand, it would be somewhat remarkable if the reaction rate bore no relation to the extent of unsaturation in the oil. Actually, under most conditions, hydrogenation will approach the character of a monomolecular reaction, the rate of hydrogenation at any instant being roughly proportional to the
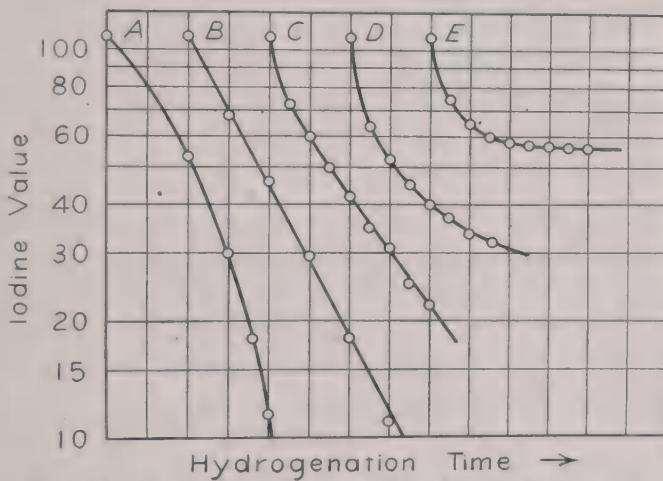
Fig. 100.   Typical cottonseed oil hydrogenation curves.

unsaturation of the oil. However, the character of the reaction is markedly influenced by various conditions of hydrogenation.

A number of typical hydrogenation curves of cottonseed oil are reproduced in Figure 100, with the logarithm of the iodine value of the oil being plotted against hydrogenation time. When so plotted, a true monomolecular or first-order reaction should yield a straight line, as in Curve B. Curves similar to Curve B are often obtained under average conditions of pressure, agitation, and catalyst concentration at moderate or low temperatures, i.e., below about 300°F. At higher temperatures, the shape of the hydrogenation curve is more inclined to resemble that of Curve C, since an increase in temperature accelerates the first stages of hydrogenation to a relatively greater extent than the latter stages, i.e., it accelerates the conversion of linoleic to oleic acid to a greater extent than the con-

version of oleic to stearic acid. In the case of Curve A, hydrogenation approaches a more nearly linear rate. This type of curve is often obtained in the hydrogenation of relatively saturated oils, such as tallow, and is also sometimes observed in hydrogenation at a low pressure with a high concentration of catalyst, where the rate of hydrogenation is determined by the rate of solution of hydrogen in the oil.

Curve D is characteristic of very high-temperature hydrogenation, of hydrogenation with a very low concentration of catalyst, or hydrogenation under conditions producing progressive slow poisoning of the catalyst during the reaction. Curve E represents a hydrogenation carried out with a self-poisoned nickel sulfate catalyst which was almost completely ineffective during the later stages of the reactions. Similar curves are obtained under conditions producing rapid catalyst poisoning.

The curves of Figure 100 were obtained with a laboratory hydrogenator of the "dead-end" type. Under fixed conditions of temperature, pressure, and catalyst concentration, the curvature of the hydrogenation curve is inclined to be greater with "dead-end" hydrogenation equipment than with "hydrogen recirculating" equipment (see Section G).

(b) Rate of Hydrogenation

Catalytic hydrogenation, like other chemical reactions, is accelerated by an increase in temperature. However, the effect of temperature on the reaction rate is somewhat less than in ordinary reactions, and is also variable. The catalyst concentration,[16] the hydrogen pressure, the degree of agitation, the kind of oil hydrogenated, and the extent to which hydrogenation is carried, will all influence the results of any series of comparative tests. Nevertheless, the curve representing hydrogenation rate plotted against temperature generally has a more or less characteristic sigmoid form. A typical curve, constructed from results obtained in the laboratory hydrogenation of cottonseed oil to an iodine value of 63.6, is shown in Figure 101. It will be seen that the over-all reaction rate increases almost exponentially in the lower range of temperatures, with a doubling interval of about 40°F. Between about 280° and 350°F. the increase becomes more nearly linear, and above 350–360°F. the rate of increase falls off rapidly, with the reaction rate apparently approaching a maximum in the neighborhood of 450°F.

However, according to Mills et al.,[16a] if hydrogenation is made to proceed very rapidly, to minimize thermal decomposition of the oil, the reaction rate will increase steadily, up to at least 260°C. (500°F.).

In the author's experience, which appears to be contrary to that of some

[16] According to R. Thomas, *J. Soc. Chem. Ind.*, *39*, 10–18T (1920), the effect of temperature should decrease as the concentration of catalyst increases.
[16a] V. Mills, J. H. Sanders, and H. K. Hawley (to Procter & Gamble Co.), U. S. Pat. 2.520.422–4 (1950).

writers, there is approximate proportionality between the hydrogenation rate and the first power of the absolute pressure—at least in the hydrogenation of vegetable oils containing oleic and linoleic acids to a plastic consistency in the range of 0–100 lbs. per square inch gage. Paterson [16b] has observed that the reaction rate varies approximately as the 1.5 power of the pressure in the hydrogenation of soybean oil. Armstrong and Hilditch[17] have pointed out that proportionality according to the first power constitutes evidence that molecular hydrogen is involved in the reaction, as with atomic hydrogen the rate would be proportional to the square root of the pressure.
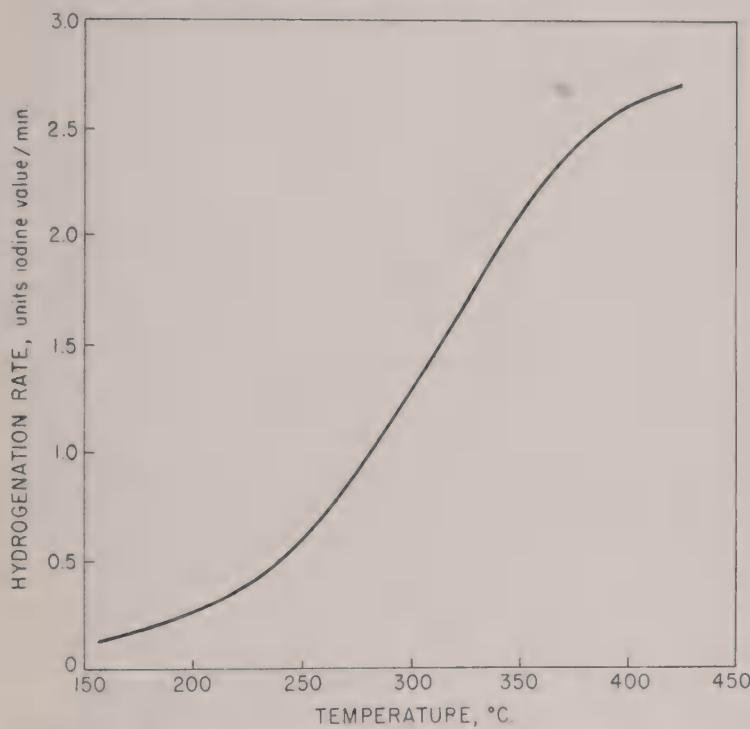
Fig. 101. Typical effect of temperature on the rate of hydrogenation.

The rate is increased as agitation of the oil mass is increased and hydrogen is increasingly dispersed; as was pointed out above, increase in the agitation above a certain level serves merely to extend the average gas–oil interface and thereby promote solution of the hydrogen in the oil. That the actual reaction of hydrogen with the oil is very rapid, but that solution of hydrogen is relatively slow was shown by the experiments of Reid and co-workers,[18] who found in a laboratory apparatus a linear in-

[16b] W. J. Paterson, quoted by J. W. Bodman, E. M. James, and S. J. Rini, Chapter XVII, in *Soybeans and Soybean Products*. K. S. Markley, ed., Interscience, 1950.
[17] E. F. Armstrong and T. P. Hilditch, *Proc. Roy. Soc.* (*London*), *100A*, 240–252 (1921).
[18] E. E. Reid and C. H. Milligan, *Ind. Eng. Chem.*, *15*, 1048–1049 (1923); F. C. Huber and E. E. Reid, *ibid.*, *18*, 535–538 (1926).

crease in the reaction rate of cottonseed oil with increase in the stirring speed, up to very high values of the latter.

Increasing the amount of catalyst causes an increase in the reaction rate, but in such a manner that building up the catalyst concentration produces steadily diminishing returns. This, of course, is to be expected from the considerations mentioned previously. With a low concentration of catalyst the oil becomes substantially saturated with hydrogen and, if the unsaturation of oil is high, the amount of catalyst becomes the factor limiting the rate of reaction. As the catayst is increased, the role of limiting factor shifts gradually from catalyst concentration to hydrogen concentration, and eventually the latter becomes so low that the rate of reaction becomes, in effect, independent of the amount of catalyst.

Hydrogenation catalysts are characterized by a strong affinity for the traces of soaps and other impurities which are found in all oils. The absorption of these has a "poisoning" effect on the catalyst, *i.e.*, the portions of the catalyst surface which combine with the impurities lose their ability to act catalytically. The concentration to which the catalyst can be reduced in practice is limited by the necessity for providing a certain amount of active nickel for the absorption of poisons. In the case of well-refined and bleached oils and active catalysts, the apparent amount of nickel poisoned by the oil is not generally greater than about $0.005-0.01\%$, calculated on the basis of the oil charge. However, unrefined or unbleached oils, or soapy oils may inactivate a much greater amount of nickel, particularly if the catalyst is not very active. Due to the tendency of the oil to poison the catalyst slightly, the speed of hydrogenation does not decrease regularly with decrease in the catalyst concentration as the latter falls to very low values. On the contrary, the hydrogenation rate falls off rapidly as the amount of catalyst approaches that required to absorb the poisons, and with any oil there is a catalyst level below which hydrogenation becomes impracticably slow. With most oils and catalysts, this level is in the neighborhood of 0.02 to 0.03%, where hydrogenation is to be practically complete, *i.e.*, where the iodine value of the oil is to be reduced to 10 to 20 units. In the case of hydrogenation involving merely the substantial elimination of acids more unsaturated than oleic, it is somewhat less, *e.g.*, 0.01%.

Under special conditions which may be achieved in the laboratory, the effect of the variables mentioned above may become more straightforward. Thus Gol'danskii and Elovich,[18a] by subjecting oleic acid in a solvent to very violent agitation with a platinum catalyst, were apparently able to attain substantial saturation of the liquid phase with hydrogen through-

[18a] V. I. Gol'danskii and S. Y. Elovich, *J. Phys. Chem. U.S.S.R.*, 20, 1085–1093 (1946).

out the reaction and over a wide range of the other operating variables. Under these conditions the rate of hydrogenation increased exponentially with the temperature (in the range 15° to 75°C.), and was directly proportional to the hydrogen pressure and to the catalyst concentration.

4. Heat of Reaction

Hydrogenation is an exothermic reaction. According to Kaufmann,[19] hydrogenation of olive oil, soybean oil, castor oil, oleic acid, etc., yields sufficient heat of reaction to raise the temperature of the oil 1.6–1.7°C. for each unit decrease in iodine value. These figures were obtained in the range of 130–200°C., and were calculated to be equivalent to approximately 25 large calories per mol per double bond saturated. The heat of hydrogenation of fatty oils is thus not very different from that of other aliphatic compounds in the liquid phase (generally 27–28 kcal. per double bond per mol).[19a]

From the best available specific heat data the temperature rise recorded by Kaufmann can be calculated to correspond to 1.6 to 1.7 B.t.u per pound per unit drop in iodine value.

5. Incidental Effects Accompanying Hydrogenation

(a) Isomerization

In the hydrogenation of fats there is a considerable tendency toward the formation of isomeric unsaturated fatty acids with properties different from the naturally occurring forms. Such isomers may originate from: (a) the addition of hydrogen at a double bond which is normally not saturated by natural processes, (b) the migration of double bonds, or (c) conversion of natural cis- to trans-forms.

Hydrogenation of the 12:13 bond in linoleic acid to form normal 9:10 oleic acid appears to be always accompanied by a minor amount of hydrogenation of the 9:10 double bond to form a positionally isomeric 12:13 acid.[20] In the hydrogenation of linolenic acid a very considerable amount of hydrogenation occurs at the middle double bond to yield an "isolinoleic" or 9:10, 15:16-octadecadienoic acid.[20,21] According to the data of Bailey and Fisher,[9,10] the hydrogen going to the middle double bond may amount to 65% of the total; hence in the hydrogenation of an oil originally high in linolenic acid, such as linseed oil, this isomer may

[19] H. P. Kaufmann, *Studien auf dem Fettegebiet*, Verlag Chemie G.m.b.H., Berlin, 1935. pp. 234–251. See also C. F. Homboe, *Ber.*, *71*, 532–541 (1938).

[19a] R. B. Williams, *J. Am. Chem. Soc.*, *64*, 1395–1404 (1942).

[20] H. van der Veen, *Chem. Umschau Gebiete Fette, Öle, Wachse u. Harze*, *38*, 89–96 (1931).

[21] H. W. Lemon, *Can. J. Research*, *F22*, 191–198 (1944).

increase to as much as 25–30% of the total fatty acids. It appears probable that "isolinoleic" acid has at least one *trans* double bond.[21a]

Comparatively little is known regarding positionally isomeric acids of hydrogenation with more than two double bonds, such as might result from the hydrogenation of marine oils. However, Lund[22] has reported the occurrence of isomers containing three as well as two double bonds in hydrogenated whale oil, and it cannot be doubted that a variety of such acids occur.

That hydrogenation may cause the migration of double bonds to new positions in unsaturated fatty acids has been established by the experiments of a number of workers. Moore,[23] Hilditch and Vidyarthi,[24] and others have found 8:9, 10:11, and 11:12 octadecenoic acids in partially hydrogenated methyl oleate or oleic acid, as well as in hydrogenated linoleates. More recently Mattil[25] and also Daubert and Filer[26] have recorded evidence that there is some shifting of double bonds to relatively widely separated positions concurrently with the hydrogenation of linoleic esters. Since the spectral method of analysis has been available for the easy detection and estimation of conjugated fatty acids it has been observed that minor amounts of such acids appear in hydrogenated vegetable oils initially devoid of conjugation. From present evidence it does not appear that double bond migration is a major factor in the production of isomeric acids, although it is undoubtedly a factor which is always operative to some degree. Apparently conjugation is at least partly independent of the addition of hydrogen, as in the presence of a hydrogenation catalyst it may be induced by heat alone.[25,27]

From a practical standpoint these isomers or new acids of hydrogenation are of interest chiefly because of their relatively high melting points and consequent effect on the consistency of the hydrogenated product. In fact, in the parlance of the industry the term "iso-oleic acid" refers simply to the unsaturated acids of high melting point which appear with the saturated acids in the conventional lead soap separation of the latter. Much uncertainty still exists regarding the identity of these acids. Presumably, however, they consist chiefly of *trans*-isomers of oleic and other octadecenoic acids, as isomerization of the variety referred to above will generally produce acids in which the double bond or bonds are nearer the free end of the fatty acid chain than in natural fats, and these

[21a] H. W. Lemon and C. K. Cross, *Can. J. Research*, B27, 610–615 (1949).

[22] J. Lund, *Fette u. Seifen*, 48, 36–65 (1941).

[23] C. W. Moore, *J. Soc. Chem. Ind.*, 38, 320–325T (1919).

[24] T. P. Hilditch and N. L. Vidyarthi, *Proc. Roy. Soc. London*, A122, 552–570 (1929).

[25] K. F. Mattil, *Oil & Soap*, 22, 213–215 (1945).

[26] B. F. Daubert and L. J. Filer, Jr., *Oil & Soap*, 22, 299–302 (1945).

[27] H. I. Waterman and C. van Vlodrop, *Rec. trav. chim.*, 57, 629–636 (1938). S. B. Radlove, H. M. Teeter, W. H. Bond, J. C. Cowan, and J. P. Kass, *Ind. Eng. Chem.*, 38, 997–1002 (1946).

are relatively low melting.[28] Various workers have isolated elaidic acid from hydrogenated fats, and Börner and Stather[29] obtained an almost pure specimen of a 10:11 acid, which had an iodine value of 88.8 and a melting point of 35.5°C. Evidence of other *trans*-isomers has been found by a number of workers.

According to Jackson and Callen,[29a] at least six different iso-oleic acids are to be found in partially hydrogenated cottonseed or soybean oils, with melting points ranging from 44 to 53°C.

Waterman and van Vlodrop[29b] have reported that in the presence of a nickel catalyst *cis-trans* isomerization can occur without hydrogenation taking place, but this is disputed by Feuge and co-workers,[30] whose results do not appear to be open to dispute, inasmuch as they were based upon an infrared spectrophotometric technique of proved reliability. The latter workers demonstrated that in *cis-trans* isomerization during hydrogenation, as in isomerization brought about by other means, an equilibrium is eventually reached (in the later stages of hydrogenation) with the monoethenoid acids consisting of approximately two-thirds *trans*-isomers and one-third *cis*-isomers. Their experiments included the hydrogenation of cottonseed oil and other commercial oils, as well as pure oleic acid esters.

In addition to its bearing upon the consistency of hydrogenated fats, the formation of the various isomers is of some concern in relation to their stability. As pointed out in Chapter II, the position of the double bonds has a great influence upon the rate at which a polyunsaturated fatty acid or its esters will oxidize. In particular, an acid with widely separated double bonds, such as the 9:10, 15:16-octadecadienoic acid referred to above, is much more resistant to oxidation than a natural acid of equal unsaturation which contains the active —CH:CH.CH$_2$.-CH:CH— group.

It is to be emphasized that "iso-oleic" acids, as determined by the conventional lead soap method, constitute in any case but an indeterminate fraction of the total amount of high-melting *trans*-acids formed. In a commercial sample of hydrogenated vegetable oil containing 13.1% "iso-oleic" acids, Swern et al.[30a] found by infrared spectrophotometry an actual *trans*-acid content of 34.2%.

[28] For example, the melting points of the *cis*-forms of various octadecenoic acids are as follows: 6:7. 30°C.; 9:10 (normal oleic). 16°C.; 12:13. 10°C. See K. S. Markley. *Fatty Acids*, Interscience, New York, 1947, p. 48.
[29] A. Börner and J. Stather. *Fette u. Seifen*, 49. 243–253 (1942).
[29a] F. L. Jackson and J. E. Callen, Abstracts of Papers, 41st Annual Meeting. American Oil Chemists' Society, New Orleans, 1950.
[29b] H. I. Waterman and C. van Vlodrop, *Rec. trav. chim.*, 57, 629–636 (1938).
[30] R. O. Feuge, M. B. Pepper, Jr., R. T. O'Connor, and E. T. Field, Abstracts of Papers, 24th Fall Meeting, American Oil Chemists' Society, San Francisco, 1950.
[30a] D. Swern, H. B. Knight, O. D. Shreve, and M. R. Heether. *J. Am. Oil Chem Soc.*, 27, 17–21 (1950).

According to Jackson and Callen,[29a] the conventional Twitchell lead soap method permits 30 to 45% of the total *trans*-monoethenoid acids to pass into the liquid acid fraction; the solubility of the lead salts of the latter is enhanced by mutual solubilization effects on the part of the several different chemical individuals involved.

(b) *Migration of Fatty Acid Radicals*

Hydrogenation is not ordinarily considered to produce any rearrangement of the fatty acid radicals within the glycerides. However, Atherton and Hilditch[31] have reported a considerable degree of acyl wandering in oils hydrogenated for prolonged periods at a relatively high temperature (180°C.), in the presence of an unstated concentration of nickel catalyst. This phenomenon is presumably to some degree independent of hydrogenation, since it was found to occur to a slight extent in oil agitated with a nickel catalyst under an atmosphere of carbon dioxide.

(c) *Other Effects*

Other effects of hydrogenation upon the glycerides and nonglyceride constitutents of fats and oils will be considered later (page 747), in dealing with the characteristics of hydrogenated oils.

D. Course of Hydrogenation

1. DIVERSITY OF POSSIBLE REACTIONS

The diversity of courses which hydrogenation may follow may be appreciated by reference to Figure 102, which represents the double bond system of a glyceride molecule containing oleic, linoleic, and linolenic acids.

$$
\begin{array}{l}
\text{H} \\
|\\
(\alpha\text{-posi-}) \quad \text{H--C--OOC(CH}_2)_7\text{CH}\overset{1}{=}\text{CHCH}_2\text{CH}\overset{2}{=}\text{CHCH}_2\text{CH}\overset{3}{=}\text{CHCH}_2\text{CH}_3 \quad \text{(linolenic)} \\
\text{tion)} \quad \quad | \\
(\beta\text{-posi-}) \quad \text{H--C--OOC(CH}_2)_7\text{CH}\overset{4}{=}\text{CHCH}_2\text{CH}\overset{5}{=}\text{CH(CH}_2)_4\text{CH}_3 \quad \quad \text{(linoleic)} \\
\text{tion)} \quad \quad | \\
(\alpha'\text{-posi-}) \quad \text{H--C--OOC(CH}_2)_7\text{CH}\overset{6}{=}\text{CH(CH}_2)_7\text{CH}_3 \quad \quad \text{(oleic)} \\
\text{tion)} \quad \quad | \\
\quad \quad \quad \text{H}
\end{array}
$$
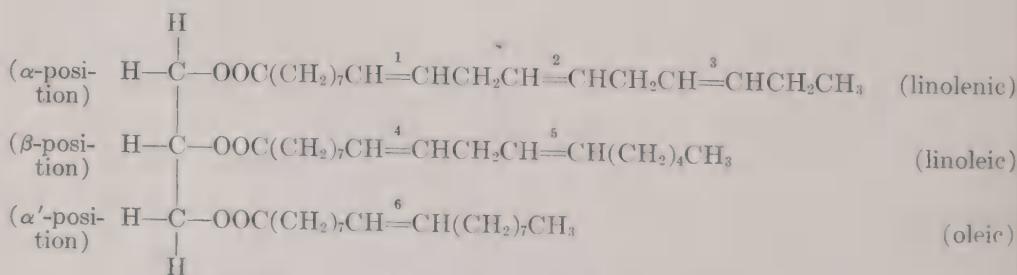
Fig. 102.   Double bond system of oleo-linoleo-linolenin.

In general, hydrogen tends to add first to the most unsaturated fatty acids.[32]   Hence, upon contact of the above molecule with hydrogen and

[31] D. Atherton and T. P. Hilditch, *J. Chem. Soc., 1941*, 527–535.
[32] There are exceptions to this rule; see page 704.

active nickel, the most probable reaction is hydrogenation at one of the double bonds of linolenic acid, to produce an oleo-dilinolein. However, there are three positions at which hydrogen may add; hence in this reaction alone there is the possibility of producing three different glycerides, according to whether saturation occurs at bond 3 or 2 or 1, to yield, respectively, normal 9:10, 12:13-linoleic acid, or its 9:10, 15:16 or 12:13, 15:16 isomers.

The above covers only what appears to be the most probable reaction. According to the best present evidence, all of the following reactions are probably also possible: (a) hydrogenation of bonds 2 and 3 simultaneously, to give normal dioleo-linolein; (b) hydrogenation of bonds 1 and 2, to give an isomeric dioleo-linolein; (c) hydrogenation at bond 5, to give normal dioleo-linolenin; (d) hydrogenation at bond 4, to give an isomeric dioleo-linolenin; (e) hydrogenation at bond 6, to give stearo-linoleo-linolenin. Similarly, the occurrence of any one of the above will still leave a multiplicity of possibilities when the second contact is made, and so on, until saturation of the glyceride molecule is virtually completed. Even after hydrogenation has become so far advanced that there are but two double bonds remaining, there will still be possibility for variation in the course of reaction, unless the two occur in a symmetrical stearo-diolein.

When it is recalled that all natural fats consist, not of one, but of a number of different glycerides, it will be appreciated that hydrogenation is too complicated and methods of analysis too inadequate for any but the main trends of the over-all reaction to be discernible.

2. Selectivity and Iso-oleic Acid Formation in Oleic-Linoleic Acid Oils

(a) Composition of Oils Hydrogenated Selectively and Nonselectively

A considerable part of the literature of hydrogenation deals with cotton-seed oil, since until quite recently this oil was predominant in the United States in the edible field. Among the more extensive investigations reported may be mentioned those of Moore, Richter, and Van Arsdel,[33] Richardson, Knuth, and Milligan,[34] Dhingra, Hilditch, and Rhead,[35] and Bailey, Feuge and Smith.[36]

In an oleic-linoleic acid oil the course of hydrogenation in terms of the

[33] H. K. Moore, G. A. Richter, and W. B. Van Arsdel, *J. Ind. Eng. Chem.*, 9, 451–462 (1917).
[34] A. S. Richardson, C. A. Knuth, and C. H. Milligan, *Ind. Eng. Chem.*, 17, 80–83 (1925).
[35] D. R. Dhingra, T. P. Hilditch, and A. J. Rhead, *J. Soc. Chem. Ind.*, 51, 195–198T (1932).
[36] A. E. Bailey, R. O. Feuge, and B. A. Smith, *Oil & Soap*, 19, 169–176 (1942).

fatty acid composition, is conveniently shown with the aid of triangular diagrams, as first proposed by Moore, Richter, and Van Arsdel.[33] Such a diagram is reproduced in Figure 103, which illustrates typical hydrogenations of cottonseed oil.[36a] In a triangular diagram representing a three-component system (in this case saturated acids, oleic acids, and linoleic acid) a mixture of any specific composition is indicated by a single point on the diagram. In this case the fatty acid composition of the unhydrogenated cottonseed oil is 25% saturated acids, 25% oleic acid, and 50% linoleic acid. Oil of this composition is indicated by the point A. If hydrogenation were wholly selective, so that complete conversion of linoleic acid to oleic acid was obtained prior to any conversion of oleic to saturated (stearic) acid, hydrogenation would proceed along line AB to point B, and then along line BC to point C, at which point the oil would
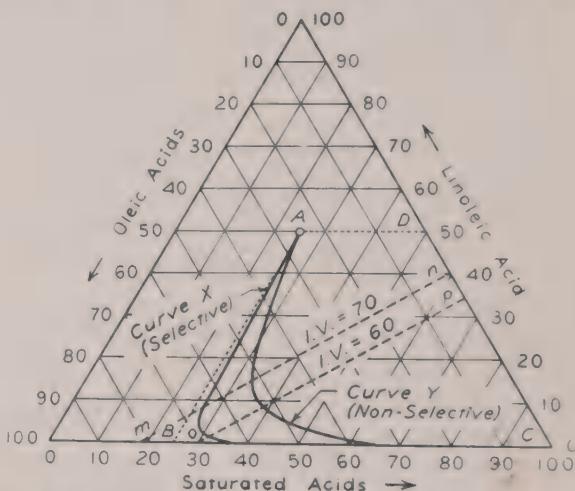
Fig. 103. Triangular diagram, showing typical changes in the composition of cottonseed oil hydrogenated selectively and nonselectively.

be completely saturated. Similarly, wholly nonselective hydrogenation would proceed along lines AD and DC. Partially selective hydrogenation is represented by any line proceeding from A to C through the area bounded by AB, BC, CD, and DA. The selectivity of the process is measured by the closeness with which the hydrogenation curve approaches corner ABC.

The actual course of hydrogenation, of cottonseed oil hydrogenated by the batch system, is represented by the typical curves, X and Y. Curve X may be considered representative of quite selective hydrogenation, whereas Curve Y represents hydrogenation decidedly lacking in selectivity. Most commercial products will be found to be intermediate in composition between X and Y. However, it is possible to hydrogenate slightly

[36a] For an alternative method of graphically representing the course of hydrogenation in terms of the composition of the oil, see Fig. 104.

more selectively and considerably more nonselectively in the laboratory under somewhat extreme conditions of temperature, pressure, agitation, and catalyst concentration.

Products having iodine values of 70 and 60, respectively, are represented in Figure 103 by the lines mn and op. A comparison of the composition of products X and Y at these two iodine values is presented in Table 112.

TABLE 112

COMPOSITION OF SELECTIVELY AND NONSELECTIVELY HYDROGENATED COTTONSEED OIL AT IODINE VALUES OF 70 AND 60

Hydrogenation conditions	Iodine values	Percentage composition of fatty acids		
		Saturated	Oleic	Linoleic
Selective	70	27.0	65.0	8.0
Nonselective	70	33.5	52.0	14.5
Selective	60	31.5	67.0	1.5
Nonselective	60	38.5	52.5	8.5

Other oleic-linoleic acid oils, such as peanut oil, sesame oil, sunflowerseed oil, corn oil, etc., hydrogenate similarly to cottonseed oil. However, the composition of the hydrogenated oil is conditioned, in all cases, by the composition of the original oil. Since the relative amounts of oleic and linoleic acids that are hydrogenated are dependent upon the concentrations of the acids as well as upon their reactivity, it follows that, in general, the greatest amounts of saturated acids are formed in the hydrogenation of the oils with the highest iodine values. This was noted as long ago as 1927 by Williams,[37] who conducted a series of tests (apparently under rather nonselective conditions), and recorded the following percentages of saturated acids formed in hydrogenating different oils to the iodine value corresponding to completely selective conversion of all polyethenoid acids to oleic:

Oil	Original I.V.	Sat. acids formed, %
Linseed	185.5	15.0
Soybean	142.0	10.5
Corn	125.0	8.5
Cottonseed	114.1	7.0
Peanut	94.2	5.5

The analyses in Table 113 furnish an idea of the differences in composition between cottenseed oil and peanut oil hydrogenated under identical conditions to a common iodine value.

[37] K. A. Williams, *J. Soc. Chem. Ind.*, *46*, 446–448T (1927).

COMPARISON BETWEEN COTTONSEED OIL AND PEANUT OIL HYDROGENATED UNDER
IDENTICAL CONDITIONS TO AN IODINE VALUE OF 65

Oil	Hydrogenation conditions	Percentage composition of fatty acids		
		Saturated	Oleic	Linoleic
Cottonseed	Moderately selective	31.5	64.5	4.0
Peanut	Moderately selective	27.5	72.5	nil
Cottonseed	Nonselective	36.0	56.0	8.0
Peanut	Nonselective	30.0	67.0	3.0
Cottonseed	Very nonselective	39.5	48.5	12.0
Peanut	Very nonselective	33.0	61.0	6.0

The content of linoleic acid in hydrogenated oils is a matter of considerable moment, inasmuch as the stability of the oil is dependent largely
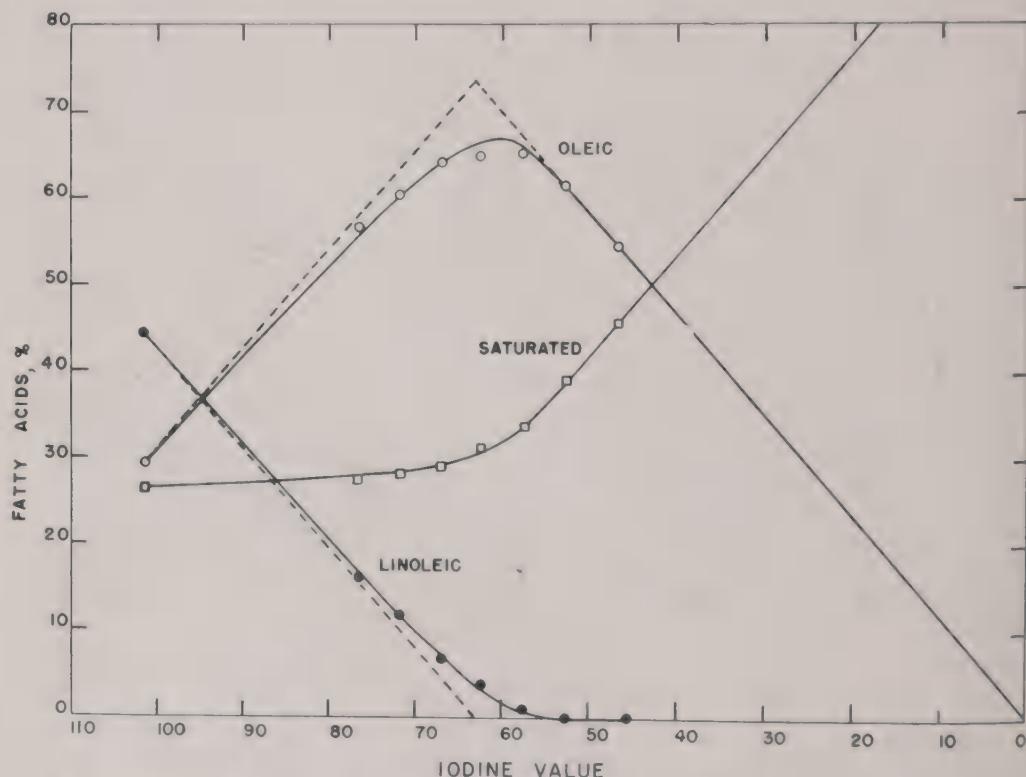
Fig. 104. Selective hydrogenation of cottonseed oil: plotted points represent experimentally determined composition; solid lines represent composition calculated, with reaction rate of linoleic acid taken as 38 times reaction rate of oleic acid. (Hypothetical composition with perfect selectivity of hydrogenation is shown by broken lines, for comparison).[10]

upon the content of this acid, rather than upon the over-all degree of unsaturation (see pages 250–254). Hydrogenated oils tend to be lowest in

linoleic acid when the ratio of linoleic to oleic acid is low originally; in this respect cottonseed oil is in a less favorable position than some other vegetable oils. The influence of raw oil composition on the composition of the hydrogenated product at specific iodine values and consistencies is discussed in more detail in Chapter VIII.

In hydrogenated linolenic acid oils the same general considerations apply, but the picture is somewhat complicated by the fact that linolenic acid may hydrogenate to form either normal 9:10, 12:13-linoleic acid or the considerably different 9:10, 15:16 isomer. The composition of these oils after hydrogenation will be considered later.

Bailey[10] has shown that the composition of an hydrogenated oil over a range of iodine values corresponds very closely to that calculated by assuming that the relative reaction rates of the different component fatty acids do not change during the reaction. In Figure 104 is shown a typical comparison between actual compositions and calculated compositions for a selectively hydrogenated cottonseed oil, calculation being made upon the assumption that the reaction rate of linoleic acid was 38 times that of oleic acid.

(b) Development of Iso-oleic Acids

In all of the preceding discussion reference has been made only to oleic acid, without distinction between normal oleic acid and the higher melting iso-oleic acids formed during hydrogenation.

There are valid objections to dealing with the iso-oleic acid content of a hydrogenated fat in completely quantitative terms. As indicated previously, the term iso-oleic acids, as used by the fat technologist, refers simply to the unsaturated acids that are precipitated along with the saturated acids in the course of a conventional lead salt separation. The solubilizing effect of other unsaturated acids upon the iso-oleic acids or their salts is undoubtedly great. In any case, the percentage of iso-oleic acids as determined is certainly less than the total percentage of high-melting isomers in the fat, and probably the proportion of the total recovered is dependent upon the composition of the sample, being greatest at low iodine values when relatively small proportions of other unsaturated acids are present. Iso-oleic acid determinations thus furnish a valid basis for the comparison of different fats at roughly equivalent iodine values, but it should be emphasized that they have serious limitations in any application where absolute values are required (see page 689).

The typical manner in which iso-oleic acids are developed during the hydrogenation of an oil is illustrated in Figure 105, which is taken from the data of Fisher et al.[37a] on selectively hydrogenated peanut oil. The

[37a] G. S. Fisher, R. T. O'Connor, and F. G. Dollear, *J. Am. Oil Chem. Soc.*, *24*, 382–387 (1947).

iso-oleic acids, like the total oleic acids, rise to a maximum and then de-
cline as hydrogenation progresses. The maximum lies at a somewhat lower
iodine value than the maximum for total oleic acids (usually at an iodine
value of 50–55 for either cottonseed or peanut oil, and somewhat higher
for soybean oil, corn oil, etc.). The reason for the lower maximum may be
presumed to lie in part in the fact that iso-oleic acids may be produced
from preformed oleic acid, and hence that the formation of these acids does
not necessarily cease after all linoleic acid has disappeared. In part, it
may be due to a tendency for the isomeric acids to hydrogenate less
readily than normal oleic acid. It has been observed[38] that *trans*-isomers
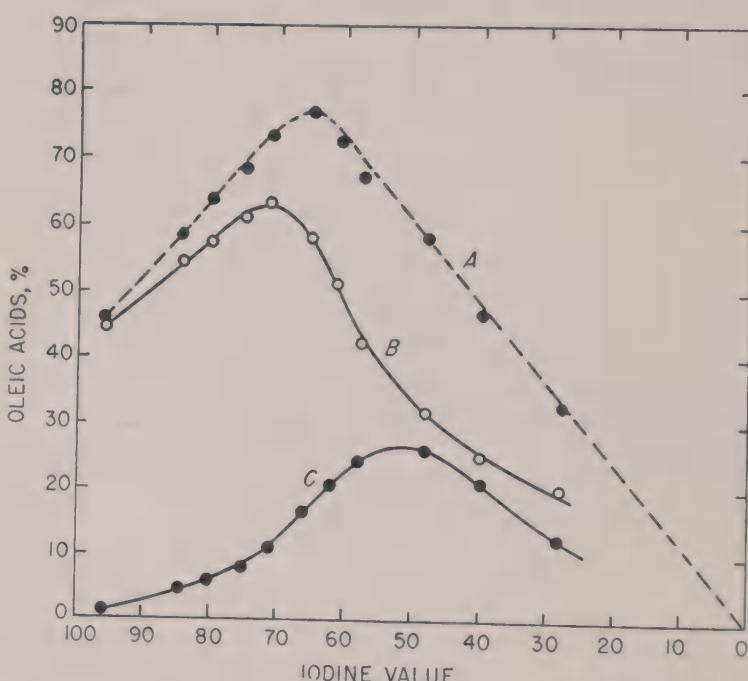
Fig. 105. Development of different monoethenoid acids during
the selective hydrogenation of peanut oil: (*A*) total oleic acids,
(*B*) normal oleic acid (by difference), (*C*) iso–oleic acids.

undergo oxidation, halogenation, mercuration, etc., less readily than the
corresponding *cis*-isomers. In part, it may be an artifact, arising from a
deficiency in the analytical method for iso-oleic acids which leads to a
less complete recovery of the latter at high iodine values (see above).

The maximum iso-oleic acid content will vary greatly according to the
conditions of hydrogenation; the data of Figure 105 were obtained under
conditions conducive to relatively extensive isomerization. In oils such
as cottonseed, peanut, or soybean, hydrogenated with normal catalysts,
it may be as low as 4–5% or as high as about 30%. In the hydrogenation

[38] T. Connor and G. F. Wright, *J. Am. Chem. Soc., 68,* 256–258 (1946).

of oils with high-sulfur catalysts, iso-oleic acid contents as high as 53.5% have been reported.[38a] Different nickel catalysts have the ability to produce iso-oleic acids to considerably different degrees. With a given catalyst, the degree to which iso-oleic acids are produced is, in general, in direct proportion to the selectivity of the reaction.

(c) Influence of Temperature

Over the ordinary range of hydrogenation temperatures, increasing the temperature has a relatively greater effect upon the conversion of linoleic to oleic acid than upon the conversion of oleic to stearic acid. Hence, selectivity is enhanced by increasing the temperature. The temperature at which hydrogenation is carried out also has a marked influence upon the formation of iso-oleic acids, greater quantities of these acids being produced at higher temperatures. The data of Table 114 illustrate the effect of temperature on the composition of cottonseed oil hydrogenated under constant conditions of pressure, agitation, catalyst concentration, etc.

TABLE 114

COMPARISON OF COTTONSEED OIL SAMPLES HYDROGENATED TO IODINE VALUE OF 62.9 AT DIFFERENT TEMPERATURES, BUT WITH OTHER CONDITIONS OF HYDROGENATION CONSTANT (LABORATORY HYDROGENATIONS)[a]

Temp., °F.	Hydrogenation Time, min.	Percentage composition of fatty acids			
		Satd.	Iso-oleic	Oleic	Linoleic
250	72	39.6	8.5	39.3	12.6
300	31	34.1	11.2	47.5	7.2
350	19	32.5	14.3	47.6	5.6
Composition of oil before hydrogenation:		26.9	—	27.1	4.60

[a] A. E. Bailey, R. O. Feuge, and B. A. Smith, *Oil & Soap, 19,* 169–176 (1942).

(d) Influence of Pressure and Agitation

The effects of pressure and agitation on the fatty acid composition of hydrogenated oils are evident from the laboratory experiments on cottonseed oil which are detailed in Table 115. In these experiments the agitation was varied by simultaneously altering the speed of stirring and the size of the oil charge, the highest degree of agitation being obtained, of course, with the highest speed and the smallest charge. It may be noted that increasing the agitation decreases the selectivity, and also inhibits iso-oleic acid formation, and that increasing the pressure has the same effect as increasing the agitation.

[38a] N. W. Ziels and W. H. Schmidt (to Lever Bros. Co.), U. S. Pat. 2,468,799 (1949).

TABLE 115

Comparison of Cottonseed Oil Samples Hydrogenated to Iodine Value of 62.9 at Different Pressures, But with Other Hydrogenation Conditions Constant, and Hydrogenated with Different Degrees of Agitation, But with Other Conditions Constant (Laboratory Hydrogenations)[a]

Pressure, lbs./sq. in. gage	Agitation		Catalyst concn., % nickel	Satd. Hydrogenation time, min.	Percentage composition of fatty acids			
	R.P.M.	Lbs. oil			Iso-oleic		Oleic	Linoleic
5	408	12	0.05	67	32.8	13.2	48.1	5.9
27	408	12	0.05	31	34.1	11.2	47.5	7.2
50	408	12	0.05	21	35.2	10.2	46.2	8.4
27	290	16	0.10	101	31.7	15.8	47.7	4.8
27	408	12	0.10	24	32.8	12.4	48.9	5.9
27	528	8	0.10	12	34.2	10.7	47.8	7.3

[a] A. E. Bailey, R. O. Feuge, and B. A. Smith, *Oil & Soap, 19*, 169–176 (1942).

(e) Effect of Catalyst Concentration

Increasing the concentration of a given catalyst, with other factors constant, has the effect of making the reaction more selective and increasing the concentration of oleic acids. This is illustrated by the experiments shown in Table 116.

TABLE 116

Comparison of Cottonseed Oil Samples Hydrogenated to Iodine Value of 62.9 with Different Concentrations of Same Catalyst, But with Other Hydrogenation Conditions Constant (Laboratory Hydrogenations)[a]

Catalyst, concn., % nickel	Hydrogenation time, min.	Percentage composition of fatty acids			
		Satd.	Iso-oleic	Oleic	Linoleic
0.025	98	35.1	11.0	45.7	8.2
0.050	31	34.1	11.2	47.5	7.2
0.100	24	32.8	12.4	48.9	5.9

[a] A. E. Bailey, R. O. Feuge, and B. A. Smith, *Oil & Soap, 19*, 169–176 (1942).

(f) Effect of Nature of the Catalyst

As indicated previously, some nickel catalysts are naturally more selective than others, *i.e.*, they tend to produce relatively large amounts of saturated acids and large amounts of iso-oleic acids simultaneously. Typical differences among catalysts are illustrated in Figure 106, which shows laboratory results in which hydrogenation conditions were varied in such a manner as to give varying degrees of selectivity for the reaction.[39]

[39] A. E. Bailey, *J. Am. Oil Chem. Soc., 26*, 596–601 (1949).

Partial poisoning tends to render a catalyst nonselective, and hence catalysts undergo a progressive loss in selectivity with repeated use. The presence of sulfur compounds in a catalyst (introduced, for example. when the catalyst is prepared from nickel sulfate) produces a self-poisoning effect and a nonselective catalyst. Consequently, lack of selectivity
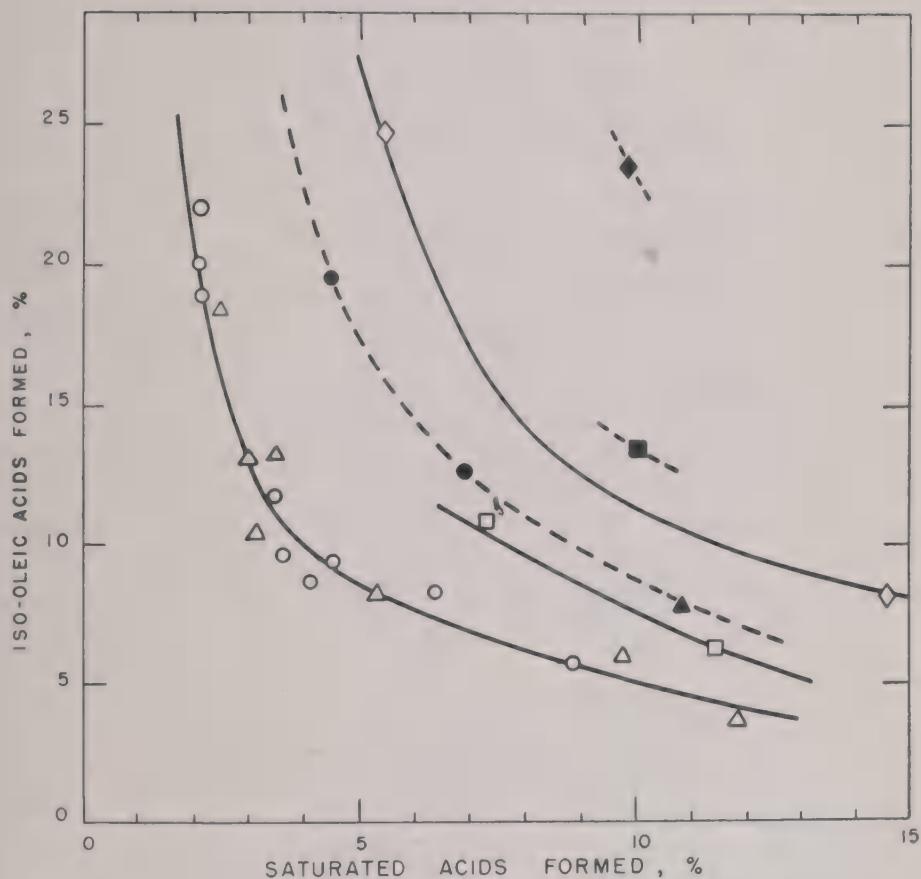
Fig. 106. Saturated acid formation *vs.* iso-oleic acids formation in the hydrogenation of cottonseed oil to an iodine value of 65 with different catalysts: open circles, catalyst A; open triangles, catalyst B; open squares, catalyst C; open diamonds, catalyst D; closed circles, catalyst A used in very low concentration (0.01% nickel); closed triangles, catalyst B, low concentration; closed squares, catalyst C, low concentration; closed diamonds, catalyst D, low concentration. (Catalyst was precipitated from nickel sulfate and high in sulfur content).[39]

is often associated with a high sulfur content. However, considerable differences in selectivity may exist in catalysts completely free of sulfur.

Richardson and Snoddy[39a] observed that platinum catalysts hydrogenated with much less selectivity than nickel catalysts under compa-

[39a] A. S. Richardson and A. O. Snoddy, *Ind. Eng. Chem.,* 18, 570–571 (1926).

rable conditions of hydrogenation, and with the production of less iso-oleic acids.

In considering the behavior of different nickel catalysts, it must be borne in mind that comparisons between two different catalysts on the basis of their total nickel contents are valid only if the two are of equal activity. Only a small proportion of the total metal in a catalyst is actually catalytically active, the remainder being altogether inert. The important characteristic of a catalyst is not its total nickel content, but its content of active nickel. The latter can be judged only on the basis of the activity of the catalyst. The concentration of the catalyst is one of the important variables determining the composition of the hydrogenated oil; hence in comparing two different catalysts at equal concentrations of total nickel, one may have different products simply because one of the catalysts is more active than the other.

(g) Theory of Effects of Different Operating Variables

Upon first thought, the effects of the variables enumerated above appear to be inconsistent and full of contradictions. Since linoleic acid reacts more readily than oleic acid, common sense would dictate that hydro-
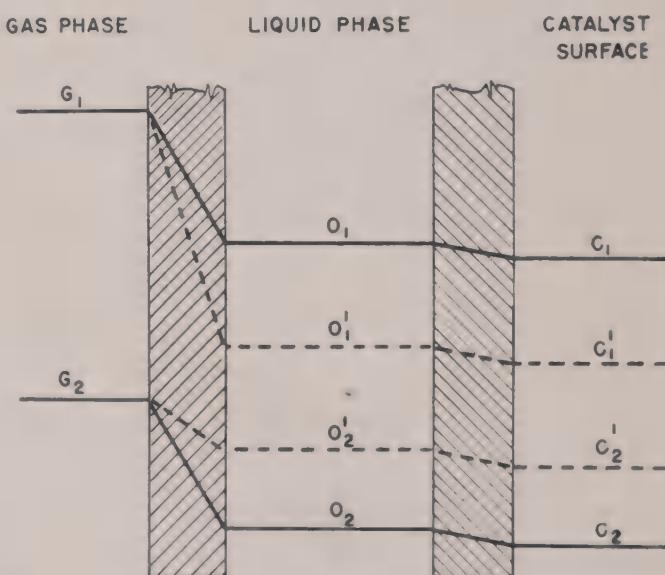
Fig. 107.   Diagrammatic representation of hydrogen concentration in the three phases of a reacting oil–hydrogen–catalyst system.[10]

genation should be carried out under the mildest possible conditions, if maximum selectivity is sought. Selectivity is, in fact, promoted by the use of low operating pressures and limited agitation or hydrogen dispersion, both of which are obviously to be classed as "mild" conditions.

However, high temperatures and high concentrations of catalyst, which likewise favor selectivity, can scarcely be placed in this category.

The observed effects of pressure, hydrogen dispersion, catalyst concentration, and temperature may be at least partially rationalized by considering the reacting system of hydrogen and unsaturated oil in terms of the concentrations of the two reactants. Selectivity appears to be favored by a low concentration of hydrogen in the actual zone of reaction, which in this case is the active catalyst surface.[10]

In Figure 107 a diagrammatic representation is given of the relative concentrations of hydrogen under different conditions in the gas phase, in the liquid phase (dissolved in the oil), and on the catalyst surface. At a given pressure, corresponding to G_1, and at a fixed temperature and catalyst concentration, there will be an appreciable concentration gradient through the film at the gas–oil interface (represented by the shaded area to the left), leading to a lowered concentration level, O_1, in the liquid, and an unknown (but possibly slight) concentration gradient (represented in the shaded area at the right), between oil and catalyst, leading to a still further lowered concentration level, C_1, on the catalyst surface. Lowering the pressure to reduce the concentration in the gas phase, e.g., to G_2, will, of course, simply displace the entire concentration curve downward, to a new series of levels, G_2, O_2, and C_2. Increasing the gas–liquid interface, through the application of more efficient agitation or gas dispersion, will lessen the interface gradient, raising the liquid-phase concentration from O_2 to O_2' and the concentration on the catalyst surface from C_2 to C_2'.

With constant agitation or gas dispersion and the pressure fixed to maintain the gas-phase concentration of hydrogen at the level of G_1, an increase in the amount of catalyst will serve to take dissolved hydrogen out of the oil more rapidly by reaction, increasing the concentration gradient in the gas–liquid interface, and reducing the concentration in the liquid and on the catalyst to the levels of O_1' and C_1', respectively. Whether an increase in the amount of active nickel available as an adsorbent will materially alter the degree to which C_1' departs from an equilibrium with O_1' cannot be determined. However, if there is any change in the concentration gradient between the oil and the catalyst surface, the gradient can only become greater, i.e., the effect brought about by increasing the catalyst can only be enhanced.

Qualitatively, the effect of an increase in temperature must be the same as the effect of increasing the amount of catalyst. In other words, it is immaterial whether impoverishment of the oil with respect to dissolved hydrogen results from the presence of more catalytically active centers or an increased rate of reaction of a fixed number of centers; either will decrease the concentration of adsorbed hydrogen. However, it is con-

ceivable that a given adsorbed hydrogen concentration at one tempera-
ture may not be altogether equivalent to the same concentration at another
temperature—the nature of the reaction may be affected by the tempera-
ture *per se,* or a few active centers functioning rapidly at a high tem-
perature may not give the same reaction products as many active centers
functioning less rapidly at a lower temperature. Limited experimental
data[10] indicate that this may not be the case and that hydrogen concen-
tration alone may be the decisive factor; however, this is by no means
proved.

It is not altogether clear just why selective hydrogenation should re-
sult from a low concentration of hydrogen on the catalyst surface and
nonselective hydrogenation from a contrary condition, even though super-
ficially it would seem that a limited supply of hydrogen should logically
go to the more reactive fatty acid radicals.

As an alternative explanation of the effect of pressure, agitation, and
catalyst concentration, but not of temperature, it may be postulated that
the action of the catalyst varies according to the rate at which it operates,
with a low rate being conducive to high selectivity and high iso-oleic acid
formation. The catalyst functioning rate is of course quite unrelated to
the rate of hydrogenation, *per se,* since with a low concentration of catalyst
each catalytically active particle may be functioning rapidly, and yet
there may be so little catalyst that the iodine value of the oil will fall
relatively slowly. Conversely, hydrogenation may be rapid, yet if the
concentration of catalyst is very high, there may be relatively long in-
tervals between the moments when each active particle actually partici-
pates in the reaction.

The relation of the rate of catalyst functioning to the composition of the
hydrogenated oil is illustrated in Table 117. In this table all data from
Tables 114, 115, and 116 have been collected, where these apply to hydro-
genations with the same catalyst at a single temperature (300°F.), and
the catalyst functioning rate has been calculated in terms of iodine units
reduced per minute per 1% of catalyst. Allowance has been made for the
inactivation of catalyst by poisons in the oil by arbitrarily assuming that
0.015% nickel is taken out of the reaction in this manner. Thus upon
the basis of this assumption, 0.100% nickel is corrected to 0.085%,
0.050% nickel is corrected to 0.035%, and 0.025% is corrected to 0.010%.
This correction seems reasonable on the basis of the behavior of the
catalyst in this series of runs, and of past experience with similar catalysts,
and appears sufficiently accurate for the illustrative purposes of the table.

It is evident from Table 117 that the hydrogenation time is not in itself
a factor in determining the composition of the hydrogenated product.

TABLE 117

RELATION OF CATALYST FUNCTIONING RATE TO COMPOSITION OF COTTONSEED OIL
HYDROGENATED TO 65.7 IODINE VALUE

(Laboratory hydrogenation at 300°F. with a nickel catalyst.)

Run no.	Catalyst concn., % nickel[a]	Hydrogenation time, min.	C.F.R.[b]	Percentage composition of fatty acids			
				Satd.	Iso-oleic	Oleic	Linoleic
23	0.285	190	0.7	31.0	20.4	44.6	4.0
11	0.085	101	4.4	31.7	15.8	47.7	4.8
19	0.035	67	15.9	32.8	13.2	48.1	5.9
15	0.085	24	18.3	32.8	12.4	48.9	5.9
12	0.035	31	34.4	34.1	11.2	47.5	7.2
9	0.085	12	36.5	34.2	10.7	47.8	7.3
16	0.010	98	38.1	35.1	11.0	45.7	8.2
17	0.035	21	50.8	35.2	10.2	46.2	8.4

[a] Corrected value; 0.015% subtracted from actual value as allowance for catalyst poisoned by impurities in the oil.

[b] Catalyst functioning rate, expressed in terms of iodine units reduction in oil per minute per 1% catalyst.

(h) Selectivity and Iso-oleic Acid Formation in Practice

Table 118, taken from unpublished work of the author and associates, shows the possible variations in composition in hydrogenating cottonseed oil in the laboratory under a somewhat wider range of hydrogenation conditions than those of the preceding tables. This table will also illustrate the preceding discussion of the effect of hydrogenation conditions and different catalysts upon the composition of the hydrogenated oils and their physical properties. It may be mentioned that the analytical values, like most of those in the other tables, are interpolated values based upon hydrogenation of the oil to the so-called "critical iodine value" as defined by Williams,[37] i.e., to the iodine value at which all linoleic acid would have been converted to oleic acid, had the reaction been completely selective. It should also be mentioned that the micropenetrations recorded in the last column constitute a measure of the consistency of the fat at the specified temperature (the greater the penetration, the softer the fat), and that the micropenetration of the average commercial shortening at this temperature is about 60–65. Catalyst Z, used for runs 15–18, was a high-sulfur catalyst precipitated from nickel sulfate solution.

For additional information on the composition of hydrogenated oleic-linoleic acid oils, reference may be made to Chapter VIII.

A recent patent[39b] claims unusual suppression of iso-oleic acid formation and saturated acid formation simultaneously by hydrogenation in the presence of an inert fat solvent. However, from the examples cited, it does not appear that the results are essentially different from those ob-

[39b] J. H. Sanders (to Procter & Gamble Co.), U. S. Pat. 2,520,440 (1950).

tainable (see Table 118) by suitable adjustment of the factors of temperature, pressure, and agitation without the presence of a solvent.

TABLE 118

COMPOSITION AND CONSISTENCY OF COTTONSEED OIL HYDROGENATED IN LABORATORY UNDER DIFFERENT CONDITIONS TO IODINE VALUE OF 63.6

Run No.	Cata- lyst	Ni, %	Temp., °F.	Pres- sure, p.s.i.g.	Agita- tion	Time, min.	Fatty acid composition, %				Micro- pen., 22.5°C.
							Satd.	Iso- oleic	Oleic	Lin- oleic	
1	V	0.05	275	5	High	110	30.2	10.5	55.2	4.1	100
2	W	0.08	275	60	High	9	31.1	9.9	54.0	5.0	81
3	X	0.05	275	5	High	45	31.1	12.4	51.5	5.0	89
4	X	0.10	350	60	Low	64	30.2	11.1	54.6	4.1	· 86
5	X	0.05	275	60	High	10	31.7	10.8	51.9	5.6	95
6	X	0.03	275	5	High	65	32.5	12.1	49.0	6.4	63
7	X	0.10	225	5	High	80	33.8	9.6	49.0	7.6	62
8	X	0.10	225	60	High	28	35.2	6.8	49.0	9.0	62
9	Y	0.10	275	60	Low	58	29.6	19.0	47.9	3.5	50
10	Y	0.04	275	5	High	126	35.1	8.5	46.9	8.9	52
11	Y	0.10	225	150	High	20	39.2	4.0	45.8	12.0	52
12	X	0.01	350	150	High	46	38.5	9.0	40.2	12.3	30
13	Y	0.01	350	5	High	110	31.8	21.7	40.7	5.8	32
14	Y	0.01	350	60	High	38	34.3	14.2	43.3	8.2	38
15	Z	0.03	275	60	High	31	39.3	8.5	39.1	13.1	30
16	Z	0.12	275	5	High	50	29.9	26.7	39.7	3.7	28
17	Z	0.02	375	5	High	36	30.5	29.2	35.9	4.4	28
18	Z	0.01	375	60	High	60	34.5	22.9	34.3	8.3	24
Original oil, runs 1–14 and 17					..	..	26.0	1.1	27.6	45.3	..
Original oil, runs 15, 16, and 18					..	..	24.0	1.0	25.0	50.0	..

3. SELECTIVITY AND ISOMERIZATION IN OILS CONTAINING POLYUNSATURATED ACIDS

In view of the fact that linoleic acid hydrogenates much more readily than oleic acid, it might be supposed that linolenic and other polyunsaturated acids would, in turn, be much more reactive than linoleic acid, and that it would therefore be possible to eliminate selectively and progressively such acids from an oil according to their increased degree of unsaturation. Such, however, is by no means the case.

Bailey et al.,[9,10] working with hydrogenated linseed and soybean oils, have found the relative reaction rates of the different unsaturated fatty acids, under comparatively selective and comparatively nonselective conditions, to be as listed in Table 119. The term iso-linoleic as used here refers to diethenoid acids which do not yield a conjugated system of double bonds upon isomerization with alkali, and which evidently consist principally or entirely of a 9:10, 15:16 isomer produced by the hydro-

genation of normal linoleic acid at the middle double bond. It will be seen that linolenic acid hydrogenates only about twice as readily as linoleic acid, and that iso-linoleic acid is much less reactive to hydrogenation than normal linoleic acid. Furthermore, while a change from nonselective to selective conditions has a large effect upon the relative reaction rates of linoleic and linolenic acids as a group and oleic and isolinoleic acids as a group, it has in either case but little effect upon the relative reaction rates of the two acids in the same group. It was also possible to estimate the relative proportions of linolenic acid reacting with hydrogen to produce normal linoleic acid (9:10, 12:13 or 12:13, 15:16), to produce 9:10, 15:16 iso-linoleic acid, and to produce oleic acid or other monoethenoid acid by the simultaneous saturation of two double bonds. The fractions of linolenic acid going to each of the three products in each case are also given in the table.

TABLE 119

RELATIVE REACTION RATES OF DIFFERENT UNSATURATED ACIDS
IN HYDROGENATION OF OILS CONTAINING POLYUNSATURATED
ACIDS AND FRACTIONS OF LINOLENIC ACID UNDERGOING HYDRO-
GENATION TO LINOLEIC, ISO-LINOLEIC, AND OLEIC ACIDS[a]

Acid	Linseed (nonselective)	Linseed (selective)	Soybean (selective)
Relative reaction rates			
Oleic	1	1	1
Iso-linoleic	2.5	3.85	5.0
Linoleic	7.5	31	50
Linolenic	12.5	77	100
Fraction of linolenic acid to acid indicated			
Linoleic	0.24	0	0
Iso-linoleic	0.65	0.54	0.53
Oleic	0.11	0.46	0.47

[a] A. E. Bailey, *J. Am. Oil Chem. Soc.*, *26*, 644–648 (1949).

It is noteworthy that when theoretical composition curves were calculated for the different series of hydrogenated oils, using the factors given in Table 119 and assuming these factors to be invariable throughout the reaction, the theoretical curves coincided almost exactly with experimentally determined composition values. The calculated and observed compositions of the nonselectively hydrogenated linseed oil are shown in Figure 108.

The probable reasons for the effects described above have been clarified by Hilditch,[40] who points out that the results constitute evidence that "selectivity" is restricted to compounds in which two double bonds are

[40] T. P. Hilditch, *Nature*, *157*, 586 (1946).

separated by a single CH_2 group, and that, in fact, it is probably a function of this particular grouping. Hilditch calls attention to the fact that the reactivity ratios found by Bailey for hydrogenation in the case of oleic, linoleic, and linolenic acids are strikingly similar to the corresponding ratios observed by Gunstone and Hilditch[41] for oxidation. In each case the reactivity is greatly augmented (8 to 30 times) when the appearance of a second double bond creates an active methylene group, but
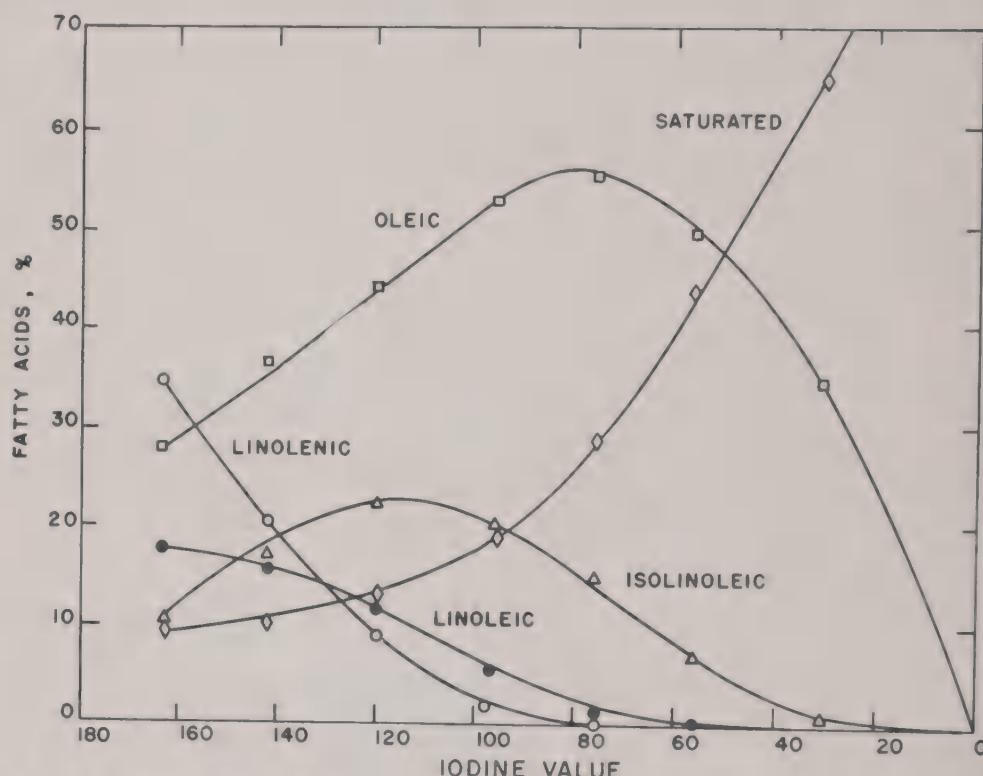
Fig. 108. Composition of nonselectively hydrogenated linseed oil, as determined by analysis, and as calculated from original composition of the oil and assumed relative reaction rates (see Table 119). Calculated composition is represented by solid lines, determined composition by plotted points.[10]

again is only doubled when a third double bond produces two such groups.

Hilditch's concept fully explains the low reactivity of the 9:10, 15:16 isomer (this isomer is also very resistant to oxidation), and also the previous observations of Richardson, Knuth, and Milligan,[14] Hilditch and Terleski,[42] and Harper and Hilditch[43] relative to the hydrogenation of marine oils. In these oils the highly unsaturated C_{20} and C_{22} acids are reduced with difficulty beyond two double bonds, considerable amounts

[41] F. D. Gunstone and T. P. Hilditch, *J. Chem. Soc.*, *1945*, 836–841.
[42] T. P. Hilditch and J. T. Terleski, *J. Soc. Chem. Ind.*, *56*, 315–322T (1937).
[43] D. A. Harper and T. P. Hilditch, *ibid.*, 322–329 (1937).

of diethenoid acids remaining even at iodine values as low as 25–30. Undoubtedly these difficultly saturated acids consist of members comparable to the 9:10, 15:16-octadecadienoate mentioned above, *i.e.*, they have widely separated double bonds and are devoid of active methylene groups.

The formation of iso-oleic acids in polyunsaturated acid oils appears to be comparable to their formation in oleic-linoleic acid oils. Additional information on the composition of hydrogenated oils of this class may be found in Chapter VIII.

4. EFFECT OF CHAIN LENGTH ON EASE OF HYDROGENATION

Acids of high molecular weight appear generally to hydrogenate less readily than lower molecular weight acids of equivalent unsaturation. Hilditch and Paul[44] have observed, for example, that erucic acid is hydrogenated with more difficulty than oleic acid.

5. EFFECT OF POSITION OF DOUBLE BOND ON ITS REACTIVITY

A double bond in a fatty acid chain appears to be increasingly difficult to hydrogenate as its distance from the carboxyl group decreases. Pigulevski and Artamonov,[44a] in a series of experiments with different octadecenoic acids and a platinum catalyst, found that the 2:3, 3:4, 6:8, and 9:10 isomers exhibited progressively increasing reaction rates. Fragmentary data on triglycerides and other esters indicate that the same rule holds with respect to combined fatty acid radicals.

6. HYDROGENATION OF OILS WITH CONJUGATED BONDS

Böeseken *et al.*[45] found that the limited hydrogenation of elaeostearic acid esters (9:10, 11:12, 13:14-octadecatrieneoates) produced esters of vaccenic (11:12-octadecenoic) acid. Vaccenic acid in yields as high as 50% was obtained by the hydrogenation of tung oil at 150–160°C. in a rotating autoclave. In a very efficiently agitated laboratory apparatus at 175°C. and atmospheric pressure some quantity of a 10:11,12:14-octadecadienoic acid was said to be produced, however.

Lemon[46] hydrogenated tung oil in a laboratory apparatus under conditions similar to those commonly obtaining in commercial practice, and examined the product spectroscopically for diene and triene conjugation, before and after alkali isomerization. There was a decrease in triene conjugation as hydrogenation progressed, but very little concurrent develop-

[44] T. P. Hilditch and H. Paul, *J. Soc. Chem. Ind.*, *54*, 331–336T (1935).
[44a] G. Pigulevski and P. A. Artamonov, *J. Gen. Chem. U.S.S.R.*, *12*, 510–517 (1942).
[45] J. Böeseken, J. van Krimpen, and P. L. Blanken, *Rec. trav. chim.*, *49*, 257–266 (1930).
[46] H. W. Lemon, *Can. J. Research*, *F25*, 34–43 (1947).

ment of diene conjugation. Further, alkali isomerization had little effect on the amount of either diene or triene conjugation present.

From the above it would appear that in the hydrogenation of elaeosteric acid the two outside double bonds are saturated simultaneously. This conclusion is in harmony with the mechanism observed by Farmer and Galley[11] in the hydrogenation of conjugated long chain compounds other than fatty esters. Hilditch and Pathak[12] confirmed the results of the preceding workers, and in addition established that in selective hydrogenation the conjugated triene group of methyl elaeostearate hydrogenates about twice as readily as the nonconjugated triene group of methyl linolenate, and much more readily than the nonconjugated diene group of methyl linoleate.

7. SELECTIVITY WITH RESPECT TO DIFFERENT CLASSES OF GLYCERIDES

Bushell and Hilditch[47] have investigated the hydrogenation process with respect to selectivity (in the hydrogenation of glycerides) and have concluded that triunsaturated glycerides hydrogenate somewhat more readily than diunsaturated glycerides, and that the latter, in turn, are somewhat more easily reduced than monounsaturated glycerides. There is a considerable tendency, however, for hydrogenation of the two to occur simultaneously. This tendency is illustrated by the results of their experiments in the hydrogenation of triolein. A fat consisting originally of triolein should, if hydrogenated with perfect selectivity to an iodine value of 32, consist of no trisaturated glycerides, 11.5% disaturated glycerides, and 88.5% monosaturated glycerides. Actually, a sample of triolein hydrogenated to this iodine value was found to consist of 15% trisaturated, 57% disaturated, and 28% monosaturated glycerides.

Contrary to the previous suggestions of Hilditch and Jones,[48] Bushell and Hilditch found that oleodipalmitin and oleodistearin hydrogenated with practically equal readiness, and that oleic acid in the a-position in the glyceride molecules was hydrogenated no more readily than that in the β-position.

The present lack of reliable methods for estimating individual glycerides, or even most classes of glycerides, makes it impossible to follow the course of hydrogenation of natural oils in terms of glycerides rather than fatty acids. However, the Hilditch technique for the estimation of fully saturated glycerides affords a reasonably satisfactory means for determining the increase in this particular class of glycerides as hydrogenation proceeds. Hilditch and co-workers have examined a number of fats during the course of hydrogenation, with respect to their fully saturated glyceride content. The data of Hilditch and Jones[48] on hydrogenated

[47] W. J. Bushell and T. P. Hilditch, *J. Chem. Soc.*, *1937*, 1767–1774.
[48] T. P. Hilditch and E. C. Jones, *J. Chem. Soc.*, *1932*, 805–820.

cottonseed oil are of particular interest. The curve of Figure 109 is constructed from the data of the latter authors.
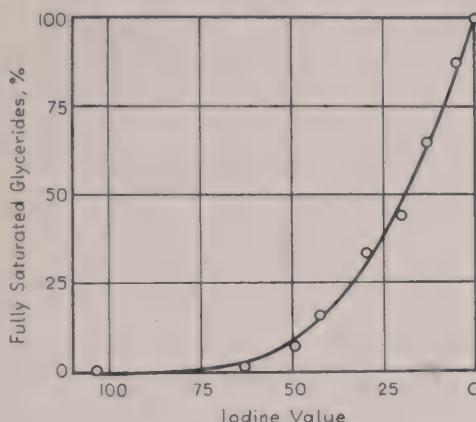
Fig. 109. Formation of fully saturated glycerides during the hydrogenation of cottonseed oil.[48]

8. Hydrogenation of Monoesters and Free Fatty Acids

The work of Hilditch and Moore[49] has shown that mixed monoesters of oleic and linoleic acids hydrogenate with the same selectivity as the
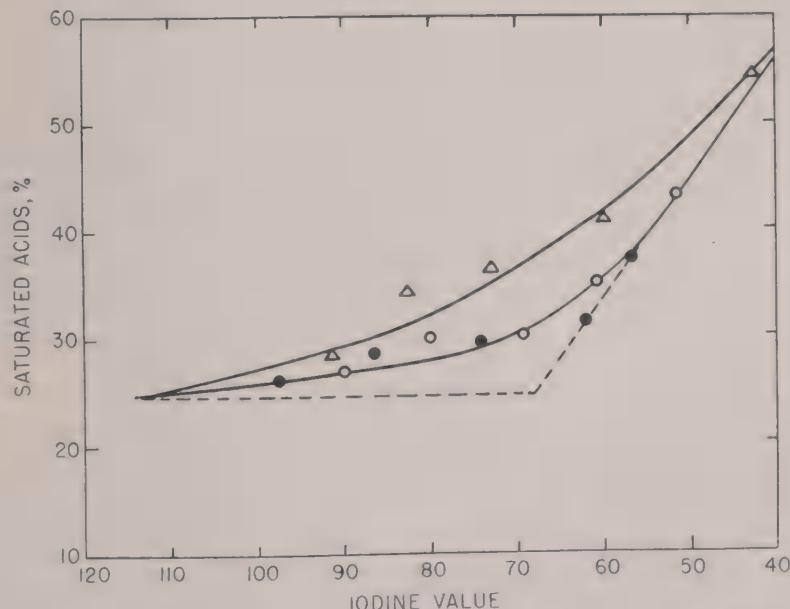
Fig. 110. Production of saturated acids in the hydrogenation at 180°C. of cottonseed oil (open circles); ethyl esters of cottonseed oil fatty acids (closed circles); and free fatty acids of cottonseed oil (triangles).[49]

[49] T. P. Hilditch and C. W. Moore, *J. Soc. Chem. Ind.*, *42*, 15–16T (1923).

mixed triglycerides of natural oils, but that much less selectivity is evident in corresponding mixtures of the free fatty acids. The comparative results of these investigators on cottonseed oil, ethyl esters of the oil, and the mixed free acids, are shown graphically in Figure 110. The lessened selectivity in the case of the latter is explainable upon the basis of the strong polarity of the free COOH groups, which become competitive with active methylene groups in the process of adsorption on the catalyst, and thus diminish the difference existing between oleic and linoleic acids in the combined form.[40]

The presence of a considerable amount of free fatty acids in an oil serves to reduce the rate of hydrogenation. According to Pelley,[50] even saturated acids can markedly reduce the reaction rate, but, on the other hand, the free acids in an oil tend to hydrogenate preferentially to the glycerides. This somewhat paradoxical effect appears reasonable if it is assumed that the carboxyl groups are adsorbed more readily by the catalyst than are unsaturated groups but are desorbed less readily.

E. Catalysts for Hydrogenation

1. Theory of Catalyst Structure

Since heterogeneous catalysis is a surface phenomenon, an essential requirement in an active catalyst is a highly extended surface. With all other factors being equal, the smaller the individual catalyst particles, the more active the catalyst will be.

In spite of the obvious relationship of surface area to catalyst activity, it does not follow by any means that the activity is determined solely by the magnitude of the surface area. The latter may be made very large without the catalyst necessarily being very active. In fact, metallic nickel dispersed to the extent of being colloidal may be virtually devoid of catalytic activity. All evidence indicates that the activity of a hydrogenation catalyst is due to a certain degree and kind of heterogeneity in the catalyst surface. The development of this heterogeneity will not occur under all conditions, but must be achieved by special methods of catalyst preparation.

The various phenomena associated with heterogeneous catalysis are best explained on the basis of the "active spots" theory of Taylor.[51] This theory assumes that the metal atoms on the surface of the catalyst possess varying degrees of unsaturation, according to the extent to which they are elevated above the general catalyst surface, or otherwise released from the mutually restraining influence of their neighboring atoms. The relatively few metal atoms which are thus highly unsaturated are the ones

[50] R. G. Pelley, J. Soc. Chem. Ind., 46, 449–454T (1927).
[51] H. S. Taylor, Proc. Roy. Soc. London, A108, 105–111 (1925).

which are capable of entering into temporary combination with the hydrogen and the unsaturated oil, in this way furthering the hydrogenation reaction. Each unsaturated atom or concentration of unsaturated atoms constitutes an active spot or center. The catalytic activity of each unsaturated atom corresponds to the extent of its unsaturation (Fig. 111).

An alternative theory of catalyst structure envisions the active portions of a catalyst as areas where the normal crystal lattice of the metal is slightly expanded, to fit more exactly the dimensional requirements for
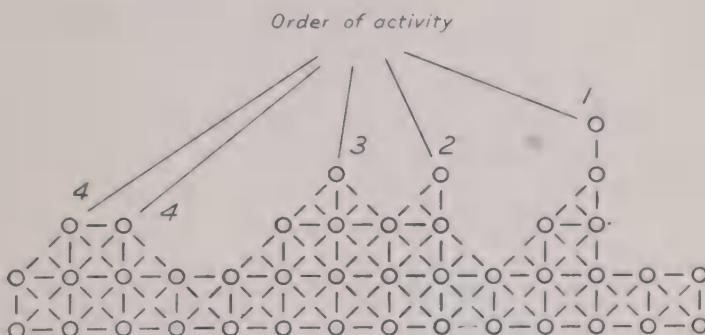
Fig. 111. Schematic representation of a catalyst surface.

two-point adsorption on either side of a double bond. In the case of nickel, the normal interatomic spacing of 2.47 Å. is actually a little smaller than the theoretical optimum. Expansion may occur as metallic nickel is produced by the reduction of a nickel compound (an expansion of 0.16 Å. has been reported in Raney nickel[51a]), or simply from reduced interatomic attraction in very small crystallites.[52]

Hydrogenation catalysts are seldom prepared directly from massive nickel, but are made by first combining the nickel with other elements, as in nickel oxide, nickel hydroxide, nickel carbonate, nickel formate, nickel-aluminum alloy, etc., and then reducing the resulting compound to regain the nickel in metallic form. The efficacy of this procedure, in producing active nickel atoms relatively free from restraint by neighboring atoms, is evident from the schematic representation of catalyst reduction in Figure 112.

It is to be noted that, according to the active spot theory, the most active nickel atoms, which are attached to the surface by the minimum of constraint, are but one step removed from a gaseous state. Armstrong and Hilditch[52a] have considered it probable that such atoms are actually momentarily detached from the catalyst during the period of their cata-

[51a] G. R. Levi and G. Rossi, *Gazz. chim. ital.*, *68*, 576–581 (1938).
[52] J. E. Lennard-Jones, *Z. Krist.*, *75*, 215–216 (1930).
[52a] E. F. Armstrong and T. P. Hilditch, *Proc. Roy. Soc. London*, A108, 111–120 (1925).

lytic functioning, and that the nickel thus actually operates in a gaseous form. The subsequent migration and attachment of the nickel atom to the most exposed part of the catalyst surface is assumed to maintain a state of average similarity to the original catalyst.

There is considerable evidence that the hydrogenation of an ethylenic compound must be preceded by two-point adsorption of the carbon atoms on either side of the double bond.[53] This requirement would impose certain dimensional limitations upon the space lattice of any catalytically active metal. Actually, the metals which are at all effective in the hydrogenation of double bonds (nickel, cobalt, iron, copper, platinum, and palladium) all have interatomic spacings close to that (2.73 Å.) calculated as optimum for such two-point adsorption.

Further discussion will be largely limited to nickel catalysts, as these are the only catalysts used in the practical hydrogenation of fatty oils.
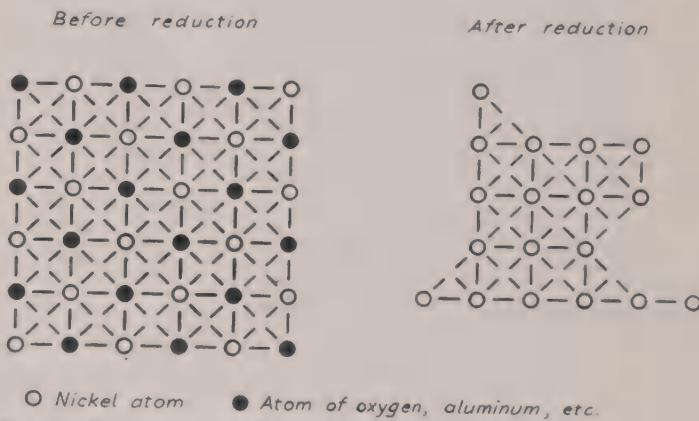
Fig. 112.   Schematic representation of effect of reduction on a nickel catalyst.

2. MISCELLANEOUS CHARACTERISTICS OF CATALYSTS

Catalysts are quite sensitive to heat, and may be rendered inactive by temperatures much below the fusion point of massive nickel. Inactivation in this case is apparently the result of a sintering process, which causes the active, projecting nickel atoms to assume more stable positions on the catalyst surface. Their sensitivity to heat makes their reduction to metallic form somewhat critical with respect to temperature, since there is usually not a large interval between the temperature at which reduction becomes rapid, and that at which sintering begins. Catalysts precipitated in the form of nickel hydroxide or carbonate on kieselguhr must usually be reduced below about 1000°F.

Freshly reduced catalysts which have not been in contact with oil are highly pyrophoric, due to the reactive nature of their unsaturated nickel

[53] See G. H. Twigg and E. K. Rideal, *Trans. Faraday Soc.*, *36*, 533–537 (1940).

atoms, and the fact that they retain much adsorbed hydrogen at the end of the reduction period. If exposed to the air at this stage of their preparation and allowed to oxidize, they are completely inactivated. Their pyrophoric properties and tendency to become inactivated through oxidation disappear, however, after the catalyst surface has become coated with oil. This behavior of catalysts is of course readily explainable on the basis of the theory of active spots or unsaturated nickel atoms.

Hydrogenation catalysts of the precipitated type are almost invariably supported on diatomaceous earth, or other porous refractory material, and other catalysts, such as those prepared by the treatment of nickel alloys, are mixed with diatomaceous earth before use. Supporting a catalyst in this manner so greatly increases its activity, and otherwise modifies its behavior, that there can be little doubt that the support contributes largely to the catalyst structure. The support appears to protect the catalyst from sintering, since supported catalysts may be successfully reduced at somewhat higher temperatures than the corresponding unsupported catalysts. It also appears reasonable to suppose that the presence of the support influences the dispersion of the catalyst particles and provides more numerous points for the attachment of unsaturated nickel atoms. In addition, there is the possibility that silica, or other material in contact with nickel, may tend to produce active nickel atoms, and hence that activity is centered at the boundaries between the nickel and the support. The latter viewpoint is quite in accord with the common observation that the activity of a metallic catalyst may be enhanced or "promoted" by the presence of another metal or metallic oxide which is not in itself a catalyst for the reaction.

3. Catalyst Poisoning

Since the activity of a catalyst depends upon the presence of a relatively few metallic atoms of an unusually high degree of reactivity, it is to be expected that these atoms will display a marked avidity for many substances other than hydrogen or glycerides, if such substances are present as impurities in the reacting system. Furthermore, if the impurities are of such a nature that they are not readily desorbed by the catalyst, but are held fast to the active atoms, they will gradually concentrate on the catalyst surface, saturating the active atoms and rendering the catalyst inactive. Substances which are thus able to cause catalysts to become inactive are termed catalyst "poisons." They may be troublesome when present even in traces in the reactants, since the amount of catalyst is always small in relation to the amount of reactants, and the active portion of the catalyst is in turn small in comparison with the total catalyst.

Catalyst poisoning may be irreversible, leading to permanent inactiva-

tion of the catalyst, or it may be reversible, if under certain conditions the poison can be removed and the original activity of the catalyst restored. Both reversible and irreversible catalyst poisoning are encountered in the hydrogenation of fats and oils.

(a) Gaseous Poisons

Among the more violent poisons for nickel catalysts are the gaseous sulfur compounds: hydrogen sulfide, carbon disulfide, sulfur dioxide, carbon oxysulfide, etc. These compounds are of considerable concern in practical hydrogenation, since they may occur as impurities in crude hydrogen prepared by the steam–iron, water gas–catalytic, or hydrocarbon reforming processes. They are rapidly absorbed by nickel catalysts, and poison the catalysts irreversibly.

TABLE 120

ACTIVITY VS. SULFUR CONTENT OF A POISONED CATALYST

Approximate active nickel content of catalyst..........................	6.5%
Experiment 1:	
Calculated percentage of total nickel combined with sulfur (as NiS)....	0.9
Residual active nickel, %...	5.6
Hydrogenation time required to reduce the iodine value of cottonseed oil	
from 107 to 25, min..	30
Experiment 2:	
Calculated percentage of total nickel combined with sulfur............	2.9
Residual active nickel, %...	3.6
Hydrogenation time, as above, min....................................	48
Experiment 3:	
Calculated percentage of total nickel combined with sulfur............	6.0
Residual active nickel, %...	0.5
Hydrogenation time as above, min.....................................	280

Experience with the sulfur poisoning of commercial nickel catalysts is in general accord with the active spot theory of catalyst structure. The amount of sulfur required to poison a catalyst is in direct proportion to the activity of the catalyst. In the case of good catalysts, however, the amount of sulfur required for complete poisoning is rather larger than is to be expected from the assumption that the active nickel comprises a relatively small part of the total surface. Although inactive catalysts may be poisoned by 0.5 to 1.0 gram sulfur per 100 grams nickel, active catalysts are not rendered substantially inoperative until they have absorbed 3.0– 5.0 grams sulfur per 100 grams nickel. If it is assumed that the sulfur is combined stoichiometrically with the nickel, to yield NiS, the above amounts of sulfur correspond to about 5.5–9.0% of the total nickel in the catalyst. When a single catalyst is progressively poisoned by the addition of successive portions of a sulfur-containing compound, the activity of

the catalyst after each addition corresponds closely to the residue of active nickel, as calculated from the sulfur added and the sulfur required for complete poisoning (Table 120).

Experiments of the author with the three sulfur compounds, hydrogen sulfide, carbon disulfide, and sulfur dioxide indicate that the amount of sulfur required to inactivate a given catalyst is substantially the same, regardless of the compound from which it is derived. The avidity of catalysts for the sulfur in the three compounds varies somewhat, however, and increases in the order that the compounds are named.

Besides the sulfur compounds mentioned above, the catalyst poison most likely to cause trouble in the hydrogenation of fats and oils is carbon monoxide, which is also present in small amounts in unpurified steam–iron and steam-hydrocarbon hydrogen. Carbon monoxide is absorbed more slowly than are the sulfur compounds, and poisons the catalyst reversibly. It may be removed, and the catalyst restored to its original activity, by interrupting the hydrogenation and continuing to agitate the catalyst–oil mixture under a reasonably good vacuum (about 25 in. Hg or better) for a short time.

The poisoning effect of carbon monoxide is highly dependent upon the conditions, and particularly the temperature of hydrogenation. If hydrogenation is conducted in the neighborhood of 400°F., carbon monoxide in the amount of 0.5% in the hydrogen will slow the operation to scarcely a noticeable degree. At 350°F., its effect will be much more noticeable, and at 300°F. it will not be possible to hydrogenate with hydrogen containing as little as 0.1% carbon monoxide, without frequent evacuation of the hydrogenator. At a temperature of 200°F. it is virtually impossible to hydrogenate oils with gas containing more than a few thousandths of one per cent of carbon monoxide. The poisoning effect of carbon monoxide is relatively more troublesome at low hydrogen pressures.

Most other gases which may be present as impurities in hydrogen, including carbon dioxide, nitrogen, and methane, are not catalyst poisons, although in a hydrogenation apparatus of the "dead-end" type they will of course slow the reaction if allowed to accumulate in the head space of the hydrogenator, and dilute the hydrogen therein. It has been reported[54] that nitrogen has some tendency to poison hydrogenation catalysts, but if such an effect exists at all in plant practice, it is not very marked. Small amounts of water vapor in the hydrogen appear to have no poisoning effect.

(b) Poisons in the Oil

The matter of catalyst poisoning through impurities in the oil has been discussed to some extent previously, in connection with the effect of the

[54] R. Thomas, *J. Soc. Chem. Ind.*, **39**, 10–18T (1920).

catalyst concentration on the course of hydrogenation. Not a great deal is known as to the natural oil and fat impurities which may function as catalyst poisons. Free fatty acids in small concentrations have little effect on the activity of the catalyst. The carotenoid pigments likewise appear to be devoid of poisoning tendencies since there is no correlation between the color of an oil and the readiness with which it may be hydrogenated. There are catalyst poisons (probably phosphatides) in most crude oils, however, for these oils are more easily hydrogenated after refining. In the case of some oils, *e.g.*, crude fish oil, treatment of the crude oil with a liberal quantity of active bleaching clay is as effective in removing catalyst poisons as alkali refining.

Sodium or other alkali soaps are very pronounced catalyst poisons. Sufficient soap to poison the catalyst seriously will seldom be found in vegetable oils which have been well bleached after alkali refining, but lard, edible tallow, or other light-colored animal fats which require little or no bleaching are often soapy enough after refining to cause trouble in hydrogenation. Soap is quite effectively absorbed by used catalysts which have become largely inactivated; hence in hydrogenating alkali-refined lard, etc., the expedient is sometimes adopted of giving the fat a pretreatment with old catalyst before fresh catalyst is added.

A wide variety of substances were tested for their effect on nickel catalysts by Ueno,[55] who reported the following to be poisons: soaps of potassium, sodium, lithium, magnesium, barium, beryllium, iron, chromium, zinc, cadmium, lead, mercury, bismuth, tin, uranium, and gold; copper hydroxide; ammonium molybdate; boric, arsenious, and hydrochloric acids; glycollic, lactic, hydroxystearic, oxalic, succinic, fumaric, malic, citric, and tartaric acids; sodium taurocholate; iron, zinc, lead, mercury, sulfur, tellurium, selenium, and red phosphorus; proteins, blood albumin, blood fibrin, gelatin, glycerol, lecithin, sucrose, dextrose, mannitol, starch, morphine, strychnine, amygdalin, potassium cyanide, zinc oxide, and aluminum silicate. The following were found to be without poisoning effect: soaps of calcium, strontium, aluminum, cerium, nickel, manganese, copper, silver, vanadium, thorium, and platinum; nickel acetate, butyrate, stearate, lactate, oxalate, and succinate; tungstic acid, fatty acids, nucleic acid, nickel, tin, zirconium, aluminum, copper, hemoglobin, cholesterol, squalene, and glycogen.

The effective life of a catalyst probably depends upon the extent to which it absorbs poisons from the oil. Some slight content of poisonous substances appears to be unavoidable, even in the most carefully refined oils. Even if the latter consisted of absolutely pure glycerides, it is quite possible that some degree of catalyst poisoning might occur, through the formation and adsorption of oxidation products or other degradation

[55] S. Ueno, *J. Soc. Chem. Ind. Japan*, *21*, 898–939 (1918).

products of the oil. The literature on catalyst poisoning—particularly with respect to poisons in the oil—has been reviewed in detail by Bodman et al.[55a]

Carbon monoxide is often observed to accumulate in closed hydrogenation systems, and it is generally considered to be formed by thermal decomposition of the oil. However, this compound is also a trace impurity in much commercial hydrogen, and there appears to be some doubt that there is any appreciable evolution of carbon monoxide from oil, except at quite elevated operating temperatures.

(c) Effect of Poisoning on Catalyst Characteristics Other Than Activity

Partial poisoning of a catalyst can affect other characteristics than its activity. Sulfur-poisoned catalysts, in particular, are inclined to produce large quantities of iso-oleic acids in the hydrogenated oils. Catalysts which have become partially inactivated in use produce hydrogenated fats which are higher in iso-oleic acids at a given saturated acid level or higher in saturated acids at a given iso-oleic acid level than the fats obtained with fresh catalysts.

4. WET-REDUCED CATALYSTS

One method of preparing nickel catalysts which has long been popular comprises first converting the nickel to the easily decomposable salt of an organic acid, and then decomposing the salt by heat. The latter operation, in which the nickel is reduced to the metallic form, is carried out while the catalyst is suspended in oil; hence catalysts of this type are termed "wet-reduced." In the preparation of wet-reduced catalysts, it is essential that the nickel salt be reducible at a low temperature below that at which thermal decomposition of the oil becomes pronounced. Various nickel salts have been proposed for the purpose, but the one which has found perhaps the greatest amount of practical use is the formate, prepared by treating precipitated nickel hydroxide or nickel carbonate with formic acid.

Nickel formate begins to decompose at about 300°F. by the following reaction:

$$Ni(OOCH)_2 . 2 H_2O = Ni + 2 CO_2 + H_2 + 2 H_2O$$
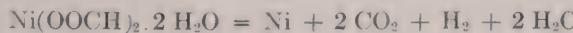
Above about 375°F. decomposition becomes rapid. Theoretically, 100 pounds of nickel formate yield 31.8 pounds of metallic nickel.

In practice, the reduction of nickel formate is carried out in specially designed closed vessels equipped with agitators, means for heating to a high temperature, and accurate temperature control. The oil in which the

[55a] See J. W. Bodman et al., footnote 1.

catalyst is suspended may be of any type, although coconut oil, or other highly saturated oil, is often preferred. The ratio of oil to nickel formate in the charge is not critical; the use of 2 to 4 parts of oil to 1 of formate is common practice. Ordinarily the rate of heating is as rapid as the design of the equipment permits. A maximum temperature in the neighborhood of 475°F. is usually employed.[56,57]

Reduction is continued for an arbitrary time, which may be upward of an hour, or until laboratory tests reveal that the product has attained the maximum activity. During the reduction period, and also during the cooling period following reduction, a slow current of hydrogen is bubbled through the oil. Since the reduction is thermal in nature, and involves no combination of hydrogen with oxygen in the catalyst, the chief function of the hydrogen is merely to sweep decomposition products out of the oil. As the catalyst becomes active, hydrogenation of the oil begins, and at the end of the reduction period it is usually completely hardened. Hugel[57] recommends that the removal of decomposition products be accomplished by maintaining a vacuum on the reducer, rather than by using a current of hydrogen.

If the catalyst is to be used in the plant in which it is prepared, the batch is cooled to about 200°F., kieselguhr equivalent to one to four times the weight of the nickel is added, and the original oil, which will have suffered some thermal decomposition, is filtered from the catalyst, and fresh oil is substituted in sufficient amount to make a fairly thick paste or slurry. Usually, the fresh oil is a liquid oil of the same kind that is to be hydrogenated.

To obtain a product that is more easily stored, shipped, and handled, chemical manufacturers usually suspend the catalyst in a highly hardened oil which may conveniently be cast into blocks, granulated, or formed into flakes over a chill roll.[57a]

Nickel formate catalysts generally have good activity and desirable characteristics with respect to selectivity and the formation of iso-oleic acids. They can be made somewhat more uniform than can dry-reduced catalysts prepared by most methods. Since the catalyst is activated while in contact with oil, the somewhat troublesome operation of transferring the reduced catalyst to oil without access to air is avoided.

The chief disadvantage of wet-reduced catalysts is that they are inclined to contain nickel particles of colloidal or near-colloidal dimensions, which are very difficult to filter from the oil after hydrogenation is completed. The formation of colloidal nickel may be minimized by careful

[56] O. H. Wurster, *Ind. Eng. Chem.*, *32*, 1193–1199 (1940).

[57] E. Hugel, in *Chemie und Technologie der Fette und Fettprodukte*. H. Schönfeld, ed., Vol. II, Springer, Vienna, 1937, p. 142.

[57a] M. L. Freed (to Seymour Mfg. Co.), U. S. Pat. 2,424,811 (1947).

attention to the reduction temperature and time, but even under the best conditions, wet-reduced catalysts are relatively difficult to filter cleanly from the oil. Oils hydrogenated with wet-reduced catalysts must usually be treated with bleaching earth or otherwise refined to insure complete removal of the catalyst, whereas good dry-reduced catalysts can in most cases be removed completely by simple filtration.

If nickel carbonate is precipitated together with copper carbonates, the resulting mixture can be reduced at a temperature sufficiently low (170–180°C.) for wet reduction to be feasible.[58] There has, in the past, been a considerable use of wet-reduced nickel–copper catalysts.

5. Dry-Reduced Catalysts

Dry-reduced catalysts are prepared by precipitating nickel hydroxide or nickel carbonate on diatomaceous earth or other refractory support, drying and grinding the precipitate, and reducing the resultant powder at a high temperature with a current of hydrogen. The preparation of dry-reduced catalysts differs fundamentally from that of wet-reduced catalysts in that the activity of the former is determined primarily in the step of precipitation, whereas the activity of the latter depends principally upon the conditions of reduction. Dry-reduced catalysts are of course finally activated by reduction, but this latter operation is relatively simple and straightforward, as compared with the highly critical process of precipitation.

(a) Catalysts by Conventional Precipitation

Since nickel sulfate is the cheapest and most readily available nickel salt, it sometimes serves as the starting material for dry-reduced catalysts. However, nickel catalysts precipitated directly from the sulfate have the property of producing excessive amounts of iso-oleic acids unless subjected to very prolonged washing for the removal of sulfates, hence for most purposes nickel nitrate is a preferable material. Nickel nitrate may be prepared directly by the action of nitric acid on the metal, or by precipitating nickel sulfate solution with an alkali and dissolving the precipitate in nitric acid.

Alkalies used for precipitating the catalyst include sodium hydroxide, ammonia, sodium carbonate, and sodium bicarbonate, with the last mentioned being perhaps the most generally suitable. Diatomaceous earth equivalent to 1 to 2 times the weight of nickel is suspended in the solution

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[58] J. Dewar and A. Liebmann, Brit. Pat. 12,982 (1913); U. S. Pats. 1,268,692 and 1,275,405 (1918).

of nickel salt at the beginning of the precipitation, to provide a support for the catalyst.

The activity of a catalyst of this type is dependent to an overwhelming degree upon such operating details as the temperature at which precipitation takes place, the rate at which the nickel salt and alkali solutions are mixed, the excess of alkali employed, the boiling to which the suspended precipitate is subjected, etc. Suitable conditions for the preparation of an active catalyst must be established by trial and error, and once they are established, it will be found that even minor deviations may affect the activity of the catalyst very greatly. In fact, even the most careful standardization of the manufacturing procedure will scarcely suffice to eliminate all variations in the catalyst; in the author's experience, at least, it is quite impossible to prepare catalysts of uniform activity by ordinary methods of precipitation. The electrolytic method of precipitation, to be described later, is recommended for the production of the most uniform and active catalysts.

The following are two methods of precipitation which have been found to yield active catalysts from nickel sulfate and nickel nitrate, respectively.

Method No. 1: 240 pounds of $NiSO_4.6H_2O$ is dissolved in 1100 gallons of distilled water, and the solution is brought to boiling. To the solution is added 60 pounds of kieselguhr. A fresh solution of 145 pounds of $NaHCO_3$ in 300 gallons of cold distilled water is made up separately, and this is added uniformly over a period of 1.0–1.5 hours to the $NiSO_4$ solution while the latter is kept continuously and vigorously boiling. There are then added 60 pounds of additional kieselguhr, and the boiling is continued for 0.5 to 1.0 hour longer. At the end of this time the solution should be slightly alkaline to phenolphthalein. The precipitated catalyst is filtered out, resuspended in 1000 gallons of distilled water, boiled for a short time, and refiltered. This last operation is repeated once or twice more, and the catalyst is then filtered, dried, and ground. It should dry to the form of a friable cake, easily disintegrated in the fingers to a fine powder of high specific volume. This catalyst requires about 8 hours reduction at 900–950°F., and contains about 24% nickel in the unreduced form.

Method No. 2: $Ni(NO_3)_2$ equivalent to 27 pounds of nickel is dissolved in 500 gallons of distilled water, and 25 pounds of kieselguhr is added. Fifty pounds of 16 Bé. sodium hydroxide and 20 pounds of aluminum powder are mixed, and after foaming has subsided, 60 pounds of sodium bicarbonate is added and the solution is made up to 300 gallons with distilled water. The latter solution is then added to the $Ni(NO_3)_2$ solution over a period of 1 hour, while the temperature of the latter is raised from about 150°F. to boiling. It is unnecessary for the aluminum to become completely dissolved during this operation. After precipitation is complete, the precipitated catalyst is filtered, resuspended in water, again filtered and resuspended, filtered, dried, and ground. This catalyst contains about 22% nickel before it is reduced and requires a temperature of about 1000°F. for reduction.

(b) Electrolytic Precipitation

A recently introduced method of catalyst preparation, which yields a product of very high activity, good characteristics, and remarkable uniformity, is that of electrolytic precipitation.[59,60] This method involves the corrosion of sheets of metallic nickel in an electrolyte by the passage of a direct current. The nickel is precipitated in the form of nickel hydroxide on kieselguhr suspended in the electrolyte.

The superiority of the electrolytic method over other methods of precipitation appears to be due to the fact that by this means the entire mass of catalyst can be precipitated at a constant and controllable pH, whereas in ordinary precipitation by the addition of one solution to another, the pH of the precipitant solution continuously varies. Furthermore, the product is unusually free of undesirable sulfur compounds. The electrolytic process, as introduced by Sieck,[59] employed an electrolyte of ammonium chloride and sodium acetate, and relied upon buffering of the electrolyte to maintain the pH of the latter within reasonable limits. However, later experience revealed that it was more satisfactory to control the pH more exactly, by the constant addition of a suitable acidic substance during the course of reaction. With the pH thus controlled, ordinary 1% sodium chloride solution, made from salt of a C.P. grade, may be substituted as an electrolyte.

The reactions occurring in the cell are as follows:

$$2\,NaCl = 2\,Na + 2\,Cl \tag{a}$$

$$2\,Na + 2\,H_2O = 2\,NaOH + H_2 \text{ (cathode reaction)} \tag{b}$$

$$2\,Cl + Ni = NiCl_2 \text{ (anode reaction)} \tag{c}$$

$$2\,NaOH + NiCl_2 = Ni(OH)_2 + NaCl \tag{d}$$
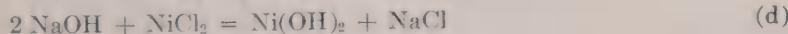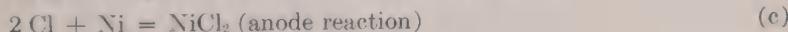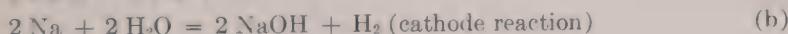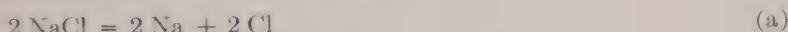
With respect to the electrolyte, the process is theoretically self-regenerative, as no sodium chloride is used up in the reaction. In practice, however, there is always formation of basic nickel chloride to some slight degree. This abstracts chloride ions from the solution, leaving an excess of sodium ions, and causes the electrolyte gradually to become alkaline. The tendency of the electrolyte to become alkaline must be counteracted by the constant addition of some acid. Gaseous carbon dioxide has been found to be a convenient acidic substance for control of the pH, being simply bubbled from a cylinder into the bottom of the cell at the proper rate during the course of operation.

A sheet of electrolytic nickel is used as the anode, and sheets or screens of the same size, made of nickel or other nonrusting metal serve as the cathodes. Low-voltage, high-amperage direct current is passed through

[59] W. Sieck, Jr., U. S. Pat. 2,054,889 (1936).
[60] W. J. Patterson (to Lever Bros. Co.), U. S. Pat. 2,123,342 (1938).

the cell at a rate sufficient to maintain a current density of approximately 55 amperes per square foot on either side of the corroded nickel sheet. The electrolyte, contained in a wooden, ceramic, or nonrusting alloy tank, is heated to 120–125°F. during the operation, and is stirred, to maintain in suspension kieselguhr equivalent to the weight of nickel to be corroded. The pH of the electrolyte is highly important, and must be maintained between about 9.0 and 9.5.

At the end of the precipitation period the catalyst is filtered out, washed free of sodium chloride with distilled water, dried, ground, and dry-reduced at 800–900°F. for 2–4 hours.

(c) Dry Reduction of Catalysts

The apparatus commonly used for the dry reduction of catalysts consists of a horizontal steel drum with conical ends, which may be slowly revolved upon its longitudinal axis. The drum is placed inside an insulated housing equipped with gas burners, which serves as a furnace. Hydrogen inlet and outlet pipes are provided to permit a current of hydrogen to be passed over the surface of the catalyst in the drum. After reduction is complete, which is usually a matter of several hours, the apparatus is cooled, the hydrogen flow is shut off, and the hydrogen inside the drum is displaced with a current of carbon dioxide. A tailpipe of large diameter attached to one of the conical ends of the drum is then uncapped, and the drum is tilted so that the reduced catalyst will discharge by gravity below the surface of oil contained in a small tank or drum. The discharge of reduced catalyst must be slow, and accompanied by intensive stirring of the oil, to prevent unwetted catalyst from floating to the surface of the oil and becoming oxidized and inactivated upon contact with the air. The slurry of oil and catalyst resulting from the above series of operations will usually contain 10–20% nickel, and may of course be added directly to charges of the same oil in the hydrogenators.

Continuous furnaces for the dry reduction of catalysts are also available from several manufacturers.[61]

6. Nickel Alloy or Raney Catalysts

A novel catalyst devised by Raney[62] has been used quite extensively, not only for the hydrogenation of fats and oils, but also for various other hydrogenation processes, both in the laboratory and in commercial operation.

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[61] See, for example, H. Sieck, *Oil & Soap*, *16*, 24–25 (1939).
[62] M. Raney, U. S. Pats. 1,563,587 (1925); 1,628,190 (1927); and 1,915,473 (1933); *Ind. Eng. Chem.*, *32*, 1199–1203 (1940). See also R. Paul, *Bull. soc. chim. France*, *7*, 296–345 (1940).

In the manufacture of Raney catalyst, nickel is first alloyed with aluminum, the most common proportions of the two metals being about 1:1 by weight. The alloy, upon cooling, is friable and easily reduced to a fairly fine powder. The catalyst is marketed in the form of such a powder.

The catalyst is prepared for use by the following procedure. In an open digestion tank is placed a considerable excess of strong (about 20%) sodium hydroxide solution. To this solution the desired amount of powdered alloy is slowly added, the rate of addition being limited by the tendency of the solution to foam out of the tank. Much heat is generated by the reaction between sodium hydroxide and aluminum, so that heating of the solution is unnecessary during the addition of the powder. Proper disposition must of course be made of the hydrogen liberated during the reaction. After the alkali solution and powder have been combined, the contents of the tank are heated to 245–250°F., and held at this temperature for 2 to 3 hours. At the end of this time the catalyst will be in the form of a sludge consisting almost entirely of metallic nickel, the aluminum being in solution in the form of sodium aluminate. The sodium aluminate and excess alkali are then removed by repeated washing with cold water, followed in each case by decantation of the wash water from the settled catalyst sludge. The washing must be very thorough, as even traces of alkali left in the catalyst will form a sufficient quantity of soap to poison it effectively when it is placed in contact with oil.

After washing is completed, the last wash water is drawn off as cleanly as possible, and the residual sludge is covered with oil. Heat is then applied, and vacuum, if it is available, to dry the sludge, and replace the protective water with oil. The catalyst is highly pyrophoric; hence it would become inactivated if dried without protection from the air. The finished catalyst is in the form of relatively large particles, and it occasions little trouble in filtration. However, kieselguhr is usually added to the oil–nickel sludge after the latter is dried. Drying of the catalyst is preferably carried out in a separate tank from that used for digestion; otherwise it is very troublesome to remove all traces of the added oil before the next batch of catalyst is digested. Any trace of oil in the digestion tank is inclined to form soaps which are highly poisonous to the catalyst.

Raney nickel produces hydrogenated oils similar to those made with good wet- or dry-reduced catalysts under comparable conditions of hydrogenation. It is often somewhat deficient in activity as compared with the best reduced catalysts, but is popular with a few hydrogenators because of the simplicity of the method by which it is activated. It avoids the use of complicated reducing furnaces, etc., and even does not require distilled water in its preparation.

7. Promotion of Nickel Catalysts

A "promoter" is a metal or other substance which has the ability to enhance the activity of a catalyst, without being in itself a catalyst for the reaction in question. The promotion of catalysts is much practiced in fields of catalysis other than the hydrogenation of fats, the employment of catalysts of two, three, four, or even more components being by no means unusual. In such complex systems the action of some of the components may more properly be described as synergistic rather than promotive, since usually more than one component will possess catalytic activity alone. However, promotion in its proper sense is very common.

A number of mechanisms have been proposed to explain the phenomenon of promotion. It has been supposed that the promoter acts as a secondary catalyst, accelerating the formation or decomposition of intermediate compounds, that it assists in the adsorption of the reactants, or that it protects the catalyst from poisons. However, in the case of catalysts for the hydrogenation of fats, it appears more reasonable to assume that the function of a promoter is simply structural, and that it permits the development of larger numbers of active centers on the catalyst surface.

Promoters play a relatively minor role in the manufacture of fat hydrogenation catalysts, since nickel catalysts of satisfactory activity can be prepared without their aid, and some of the more successful methods of catalyst preparation are not adapted to the inclusion of promoters. It is to be noted, however, that hydrogenation catalysts are commonly supported on a siliceous material, and that the latter may possibly serve as a promoter for the nickel.

One of the useful promoters for precipitated nickel catalysts is aluminum oxide. If a minor proportion of an aluminum salt is added to nickel nitrate solution before the latter is mixed with a solution of sodium carbonate, or other alkali, so that nickel and aluminum hydroxides or carbonates are coprecipitated, the resulting catalyst will usually be considerably more active after reduction than a product precipitated from nickel nitrate alone.

Other metals referred to in the patent literature as useful promoters, either as such or in the form of oxides, are chromium, colbalt, thorium, zirconium, and copper.[16a]

The mixed carbonates of copper and nickel can be reduced at a temperature much lower than that required for the reduction of nickel carbonate alone; hence in the past there has been a considerable use of copper in hydrogenation catalysts simply for its effect on the reduction temperature.[58] It has been suggested by Armstrong and Hilditch[63] that heat from the reduction of the copper produces local increases in temperature

[63] E. F. Armstrong and T. P. Hilditch, *Proc. Roy. Soc. London*, A102, 27–32 (1922).

which are sufficient to permit reduction of nickel without the average temperature of the catalyst attaining a high value.

8. Metals Other Than Nickel as Catalysts

There is at the present time probably little, if any, use of metals other than nickel for ordinary hydrogenation of fats and oils. Both platinum and palladium are effective hydrogenation catalysts, and are operative at temperatures considerably below those at which it is possible to use a nickel catalyst. However, they are less selective than nickel, and as pointed out by Richardson and Snoddy,[39] would probably be generally inferior to nickel even if their high cost did not preclude their use.

Mixed non-nickel catalysts of the metal–metal oxide type, for example, copper–chromium oxide, are recommended by Paterson[64] for hydrogenation of fats in conjunction with nickel catalysts, because of their strong decolorizing action. These catalysts are operative only at relatively high temperatures and pressure, and are normally used for the reduction of carbon-to-oxygen rather than carbon-to-carbon double bonds. However, it is claimed that the reduction of carbon-oxygen linkages in the glycerides can be made negligible by proper attention to the temperature, pressure, reaction time, etc.

Catalysts for hydrogenations of fatty materials other than the ordinary reduction of carbon-carbon double bonds will be considered in a later section under the heading of the individual hydrogenation products.

F. Hydrogen Production and Purification[65]

1. Measurement and Properties of Hydrogen

It is customary to measure commercial hydrogen in terms of standard cubic feet (SCF), defined as cubic feet of dry hydrogen at 60°F. and normal atmospheric pressure of 760 mm. of mercury or 14.70 pounds per square inch, absolute. It is to be noted that a standard cubic foot differs from a cubic foot measured at the standard laboratory temperature and pressure of 0°C. and 760 mm., 1 cubic foot at STP being equivalent to 1.057 SCF. One SCF of hydrogen weighs 0.00532 pound.

Hydrogen is highly inflammable, and readily forms explosive mixtures with oxygen or air. Mixtures of hydrogen and air are flammable when their hydrogen content by volume is greater than 4.00% but less than 74.2%. However, because of its extreme lightness, hydrogen admitted into the air tends to rise rapidly and disperse, and explosive hazard from

[64] W. J. Paterson (to Lever Bros. Co.), U. S. Pats. 2,307,065 (1943); 2,357,352 (1945); 2,437,705–706 (1948).
[65] For a review of modern hydrogen manufacturing processes, see R. M. Reed, *Trans. Am. Inst. Chem. Engrs.*, *42*, 379–401 (1946).

ordinary leakage within any adequately ventilated structure is not considered great.

2. ELECTROLYTIC PRODUCTION OF HYDROGEN

One of the oldest commercial processes for the manufacture of hydrogen, and one still much used, is the electrolytic process, wherein an aqueous electrolyte is decomposed by means of a direct current, to yield gaseous hydrogen and oxygen.

The essential parts of an electrolytic hydrogen plant are a motor–generator combination, rectifiers, or other source of direct current, a number of electrolytic cells for the actual generation of hydrogen, a hydrogen holder for receiving hydrogen from the cells, a hydrogen compressor, and high-pressure storage tanks for receiving the compressed gas. Normally, oxygen is a by-product of the process, and equipment must also be provided for receiving, compressing, and bottling the oxygen. A considerable supply of distilled water is required, for replenishment of evaporation from the cells.

Two types of cells are used. The so-called unipolar cell consists essentially of alternate metal cathodes and anodes, which usually present not more than about 20 square feet of surface each, suspended close together in a rectangular tank containing the electrolyte. For the latter a 25–30% solution of sodium or potassium hydroxide is used. Usually each cell contains but a few electrodes (in some cases but three), and hence the individual cells are relatively deep and narrow, and limited in production capacity to 20–200 cubic feet per hour each at the customary current density of about 75 amperes per square foot. The desired capacity of the complete plant is obtained by setting up the proper number of unit cells, several hundred being employed in some of the larger plants. The electrodes within each cell are usually connected in parallel; the different cells are connected in a sufficient number of series to give proper operating characteristics at the voltage supplied by the rectifiers or generator.

Diaphragms of asbestos cloth or other liquid-permeable material placed between the electrodes divert the evolved hydrogen and oxygen separately without intermixing to superimposed collecting chambers. The temperature of the electrolyte is allowed to rise to a maximum of about 170°F.; if the design of the cell is such as to permit a greater rise, the cells are cooled by external circulation of water. The cells may be either of the open or closed type, but in either the gas is collected at substantially atmospheric pressure.

Bipolar cells are sometimes referred to as cells of the filter press type, since they resemble a plate and frame press in appearance and construction. In these cells each electrode, corresponding to the plate of a filter

press, does double duty, serving on one side as the anode for one cell, and on the other as the cathode for the adjoining cell. Passage of the current is from electrode to electrode in series, from one end of the assembly to the other. Electrical connections within each cell are thus eliminated. This arrangement permits closer spacing of the electrodes and higher current densities than can be used in unipolar cells, and, hence, a generally more compact apparatus. However, there are accompanying disadvantages in the way of greater difficulties in operation and maintenance. Cells of this type have never been popular in the United States. The two types of cells are similar with respect to efficiency of hydrogen production in terms of current utilization.

Electrolytic hydrogen from the better plants usually has a purity of at least 99.8%, the impurities consisting principally of oxygen. Being quite devoid of catalyst poisons, it requires no purification before use.

The design, and to some extent the operation of an electrolytic hydrogen plant, generally involve a compromise between fixed charges determined by the investment in the plant, and operating charges for electric current. Considerable latitude is allowable in the operating conditions; the capacity of a plant of given size and cost may be increased by increasing the amperage applied to each cell. If the capacity is increased in this manner, however, there is at the same time a decrease in the efficiency of the plant, in terms of cubic feet of hydrogen produced per kilowatt-hour of current consumed.

Modern developments in the design of electrolytic hydrogen cells have been in the direction of attempts concurrently to improve the capacity and efficiency of the cells. Since the passage of a definite quantity of current will always produce the same amount of hydrogen, regardless of the type of cell, the efficiency of the latter is to be measured in terms of the voltage required for its operation. Current amounting to 1 ampere-hour liberates 0.01482 cubic foot of hydrogen measured at 0°C. and 760 mm. pressure; this is equivalent to 0.0157 SCF. Therefore, the cubic feet of hydrogen produced per kilowatt-hour of direct current is equivalent to 15.7 divided by the voltage. In the more efficient cells, the voltage required is about 2.0–2.3 volts, so that the production per kilowatt-hour is about 6.8–7.8 cubic feet. Or stated in another way, about 128–148 kilowatt-hours of current are required for each 1000 cubic feet of hydrogen produced. There is some loss (usually *ca.* 10%) in converting from alternating current to direct current; hence the over-all power consumption is in the neighborhood of 145–165 kilowatt-hours.

According to figures furnished by Taylor,[66] substantially greater economy in the way of current consumption is hardly to be expected, regard-

[66] H. S. Taylor, *Industrial Hydrogen*, Chemical Catalog Co. (Reinhold), New York, 1921.

less of possible future improvements in cell design. The theoretical decomposition potential of water, in the absence of overvoltage, is 1.23 volts, and with any form of technically feasible electrodes, the overvoltage increases this potential to not less than 1.5 volts. The necessity of providing a further potential to overcome the resistance of electrolyte and diaphragms further increases the minimum practical voltage to about 2 volts.

In the past, the electrolytic process has been favored by many hydrogenators of fatty oils because of the high purity of the hydrogen. However, this consideration is now of much less importance, since the advent of efficient purification processes for hydrogen made by other methods. The capital investment required for an electrolytic plant is relatively high, and much floor space is required. Further, except where very cheap power is available or the by-product oxygen is unusually valuable, the operating costs are usually higher than where other methods are used. It possesses the marked advantage, however, of being equally efficient in large and in small installations, and of lending itself to ready expansion in production capacity. Where a capacity of less than about 2500 cubic feet per hour is required or where cheap hydroelectric power is available it is still generally the preferred process.

3. STEAM–IRON PROCESS

A considerable part of the total hydrogen produced for fat hardening is made by the steam–iron process. In principle this process is simple, involving merely the alternate oxidation and reduction of a hot iron ore mass. Reduction is accomplished by means of the hydrogen and carbon monoxide in ordinary water gas, made by blowing hot coke with steam, or reformer gas made by reacting steam with natural gas or other light hydrocarbon. In the oxidation cycle the ore mass is blown with superheated steam, with the oxygen of the latter combining with the previously reduced ore, and the hydrogen being set free. The exact changes in the oxygen content of the iron mass in practical operation have not been fully established, but are commonly supposed to be as follows:

Reduction:

$$Fe_3O_4 + H_2 = 3\,FeO + H_2O \tag{1}$$

$$3\,FeO + 3\,H_2 = 3\,Fe + 3\,H_2O \tag{2}$$

$$Fe_3O_4 + CO = 3\,FeO + CO_2 \tag{3}$$

$$3\,FeO + 3\,CO = 3\,Fe + 3\,CO_2 \tag{4}$$

Steaming:

$$3\,Fe + 3\,H_2O = 3\,FeO + 3\,H_2 \tag{5}$$

$$3\,FeO + H_2O = Fe_3O_4 + H_2 \tag{6}$$
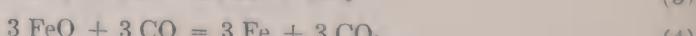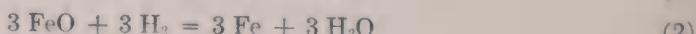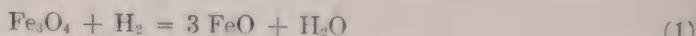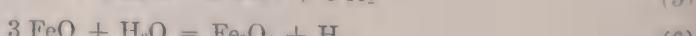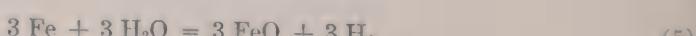
Also there is some tendency for the interaction of carbon monoxide and steam during the reduction cycle to produce carbon dioxide and hydrogen:

$$CO + H_2O = CO_2 + H_2 \qquad (7)$$

Thus carbon monoxide may either function directly as a reducing agent, or indirectly, through the production of hydrogen by the above reaction.

In addition to the above reaction, there are side reactions which do not contribute to hydrogen production, but may be mentioned because of their effect on the purity of the hydrogen. At the high temperatures prevailing in the steam–iron generator, reduced iron catalyzes the reaction:

$$2\,CO = CO_2 + C \qquad (8)$$

It is due to this reaction that there is always a slight deposit of carbon on the ore mass at the end of the reduction period. During the subsequent period of steaming any carbon thus deposited reacts with the steam to produce both carbon dioxide and carbon monoxide as impurities in the hydrogen:

$$C + H_2O = CO + H_2 \qquad (9)$$

$$C + 2\,H_2O = CO_2 + 2\,H_2 \qquad (10)$$

Water gas ordinarily contains in the neighborhood of 0.2% of hydrogen sulfide or other gaseous sulfur compounds. During the reducing phase these tend to combine with the iron contact mass, to form iron sulfide. The iron sulfide is in turn reactive with steam, so that a considerable part of the sulfur eventually finds its way into the hydrogen, in the form of hydrogen sulfide and traces of organic sulfur compounds.

In practice it will be found that carbon and sulfur will be deposited on the contact mass more rapidly than they are removed. Hence it is customary to follow each steaming period with a short period of aeration, during which air is blown through the ore to burn off carbon and sulfur accumulations. Failure to remove these accumulations is said to result in virtually complete inactivation of the contact mass.[67]

An additional source of impurities in steam-iron hydrogen reducing gas itself. After each reducing period, the generator is purged with steam for a few seconds before collection of hydrogen is begun, but this is insufficient to quite eliminate all water gas from the system. Prolonged purging is of course wasteful of hydrogen.

The composition of unpurified steam–iron hydrogen varies somewhat according to the type of generator and its mode of operation, but will ordinarily be approximately as shown in Table 121. Most of the impurities are removed in subsequent operations.

[67] S. Hurst, *Oil & Soap*, **16**, 29–35 (1939).

TABLE 121

Carbon dioxide	0.5–1.0%	Hydrogen sulfide	0.05–0.15%
Carbon monoxide	0.2–0.5%	Organic sulfur	0.1–0.5 grain per
Oxygen	0.0–0.1%		100 cubic feet
Nitrogen	0.3–1.0%	Hydrogen	98.0–99.0%

In the United States the hydrogen generator in most common use is of the Bosch or Bamag type. This generator, which is illustrated in Figure 113, consists of a single tall cylinder, lined with firebrick and insulating brick. The space within the generator is divided into two superimposed sections. In the lower section is a grate supporting the iron ore contact mass; the upper section is filled with a checkerwork of firebrick, which
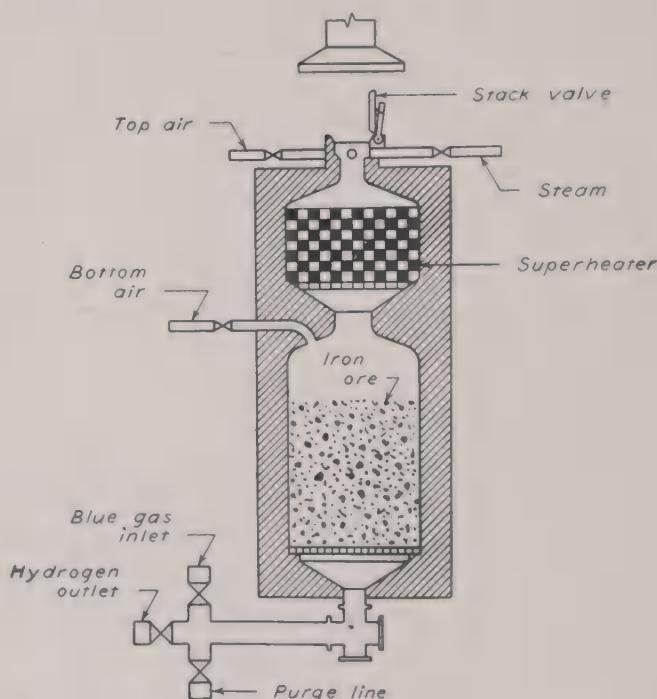
Fig. 113.   Steam–iron hydrogen generator, Bamag type.

serves as a steam superheater. Connections are provided at the extreme top of the generator for air and steam, and between the contact mass and the superheater for air. In a large line leading from the bottom of the generator is a cross, with quick-opening valves from the latter leading to a water gas inlet line, a hydrogen outlet line, and a purge line. All valves, including those mentioned above, and the stack valve, are interlocked and operated from an elevated platform near the top of the generator.

In the larger modern plants the valves are automatically opened and closed by a timing device.

The generator is operated at a temperature in the neighborhood of 1500°F., and as continuously as is feasible, since considerable time is required to warm up a cold unit. The complete operating cycle comprises the following successive operations:

Reducing.—Reducing gas is drawn from a holder and delivered to the bottom of the generator by a centrifugal blower, designed to produce a pressure of 20 to 30 inches of water. It passes up through the hot contact mass, reducing the latter, and at the bottom of the superheater meets a current of bottom air. Combustion of the partially spent gas with this air in the superheater stores up heat in the latter for the subsequent steaming period.

Purging.—The reducing gas is shut off, and hydrogen production is begun by passing steam through the superheater and then down through the contact mass. The first portions of gas are discharged through the purge line to the atmosphere, to sweep out of the system the reducing gas remaining there at the end of the reducing period.

Steaming.—The purge valve is closed, the hydrogen outlet valve is simultaneously opened, and steaming is continued. The hydrogen produced is collected.

Air blowing.—Top air is blown through the generator from top to bottom, to burn off accumulations of carbon and sulfur on the contact mass.

Reducing.—Reducing gas is again delivered to the generator, etc.

The times allowed for the different portions of the cycle are governed by considerations of economy. There is, of course, a steady diminution in the rate of hydrogen production as steaming is continued, and a similar diminution in the rate of iron oxide reduction during the reducing period. The amount of hydrogen produced during the average period of steaming is governed by the amount of reduction accomplished in the corresponding reduction period. The reduction and steaming periods are, therefore, approximately equal in length, and may together be in the neighborhood of 10 to 15 minutes. Both the purging and burning-off periods are much shorter, *e.g.*, 10–20 seconds each.

The largest single item of expense in making steam–iron hydrogen with water gas is in coke for the manufacture of the reducing gas. Water gas manufacture is a fairly well-standardized process, and the coke requirements of different plants, in terms of the volume of water gas produced, do not vary greatly. There are large differences, however, in the efficiency of hydrogen generators, depending upon their design and mode of operation. In general, practice in steam–iron hydrogen generation has improved greatly within the past 10 to 20 years. Formerly, a consumption of reducing gas amounting to 2.5–3.0 times the volume of hydrogen produced was considered good practice. In the best modern plants water gas–hydrogen ratios as low as 1.7 to 1, or even 1.5 to 1 are obtained. The latter ratio corresponds to a coke consumption of about 45 to 50 pounds per 1000

cubic feet of hydrogen. Within recent years reducing gas made by re-
forming natural gas with steam (page 735) has been substituted for water
gas in a number of steam–iron plants, with a considerable gain in operat-
ing economy.

Since the reactions represented by Equations (1) to (8) are all revers-
ible, with an equilibrium point depending upon the temperature of reac-
tion as well as the concentration of reactants, it is obvious that all of the
factors mentioned above will be affected by the temperature at which the
generator is operated, the composition of the reducing gas, and the reduc-
ing–steaming cycle adopted. A detailed discussion of the equilibria in-
volved in the manufacture of steam–iron hydrogen is furnished by Tay-
lor,[66] who particularly points out the importance of working principally
on the Fe_3O_4–FeO cycle (Equations 1, 3, and 6) rather than the FeO–Fe
cycle, Equations 2, 4, and 5) and at a relatively high temperature, in
order to obtain maximum economy in the consumption of blue gas. Ac-
tually, the reactions occurring in a steam–iron hydrogen generator are
undoubtedly more complex than as represented by Taylor or the preced-
ing equations, owing to the tendency of metallic iron and the various
iron oxides to form a continuous series of solid solutions[68] comprising
materials containing both less oxygen than FeO and more oxygen than
Fe_3O_4. In practice the utilization of both steam and blue gas is more
efficient than can be predicted from Taylor's data.

While the over-all reaction is theoretically exothermic, radiation losses
from the generator and the necessity for heating excess quantities of
steam and reducing gas require that a certain proportion of the reducing
gas be burned to maintain the temperature of the generator. Radiation
losses are greatly reduced in single unit generators, however, and par-
ticularly those of large size, in comparison with the older multiretort units.

The type of iron ore employed has an important bearing on the efficiency
of steam-iron generators. Ore from only a few localities has the requisite
properties of high reactivity and sufficient ruggedness to withstand pro-
longed use without disintegration.

The purity of steam-iron hydrogen is much less a problem now than
formerly, since methods are available for efficiently removing all of the
impurities mentioned previously, with the exception of the nitrogen. In
the better operated plants, hydrogen is now quite commonly produced
with a purity in excess of 99.5%, with the impurities consisting of nitro-
gen and methane, both of which are inert toward hydrogenation catalysts.
The individual purification processes will each be discussed in a later
section.

For additional information relative to the design of the Lane, Messer-

[68] E. D. Eastman, *J. Am. Chem. Soc.*, *44*, 975–998 (1922).

schmitt, and other types of generators, the reader is referred to the publications of Taylor,[66] Hurst,[67] and Hügel.[69] Bamag generators are commonly built in units with nominal capacities of 2500, 5000, or 10,000 cubic feet per hour.

In addition to the hydrogen generator proper, equipment required for a complete steam–iron plant includes a reducing gas generator, gas holders for both reducing gas and hydrogen, a water scrubber and cooler for the crude hydrogen obtained from the generator, air and blue gas blowers, a hydrogen compressor (if the gas is to be stored under high pressure), hydrogen storage tanks or a holder, and equipment for purifying the hydrogen.

Efficient operation of a steam–iron hydrogen plant requires metering and accounting of steam, coke, reducing gas, and hydrogen, frequent analysis of both reducing gas and hydrogen, and constant and expert attention to all operating details. Checking of the hydrogen purity is much facilitated by the ready adaptability of continuous indicators or recorders of the thermal conductivity type.

4. STEAM–HYDROCARBON PROCESS[70,71]

The steam–hydrocarbon or hydrocarbon reforming process for hydrogen manufacture has recently been developed to a high degree of perfection in the United States and has gained much favor and been widely adopted among oil and fat processors because of its economy and simplicity of operation, its flexibility, and the very high purity of the hydrogen. The latter is limited practically only by the nitrogen content of the hydrocarbon used as a raw material. The following analysis, recorded[70] for the product of a plant using liquid propane, illustrates the extreme degree of purity that is obtainable under very favorable conditions.

Carbon dioxide	0.001%
Carbon monoxide	0.001
Oxygen	0.005
Methane	0.018
Nitrogen	0.007
Hydrogen	99.968

Either commercial propane or natural gas of low nitrogen content usually serves as the raw process material, although other light hydrocarbons may be used. The hydrocarbons must be free of sulfur compounds. If the latter consist only of mercaptans, as is usually the case in

[69] E. Hügel, in *Chemie und Technologie der Fette und Fettprodukte*. H. Schönfeld, ed., Vol. II, Springer, Vienna, 1937. pp. 187–214.
[70] R. M. Reed, *Trans. Am. Inst. Chem. Engrs.*, *41*, 453–462 (1945). See also *Chem. & Met. Eng.*, *53*. No. 5, 122–123, 162–165 (1946).
[71] *Hydrogen*. The Girdler Corporation, 1946.

natural gas or propane derived from natural gas, they may be removed by scrubbing with caustic soda solution. If carbon oxysulfide or certain other organic sulfur compounds common to refinery propane are present, they must be converted to hydrogen sulfide before scrubbing is carried out, by passing the hydrocarbon vapors over a catalyst consisting of bauxite or other metallic oxide at about 700°F.

Metered amounts of steam and the desulfurized hydrocarbon vapor
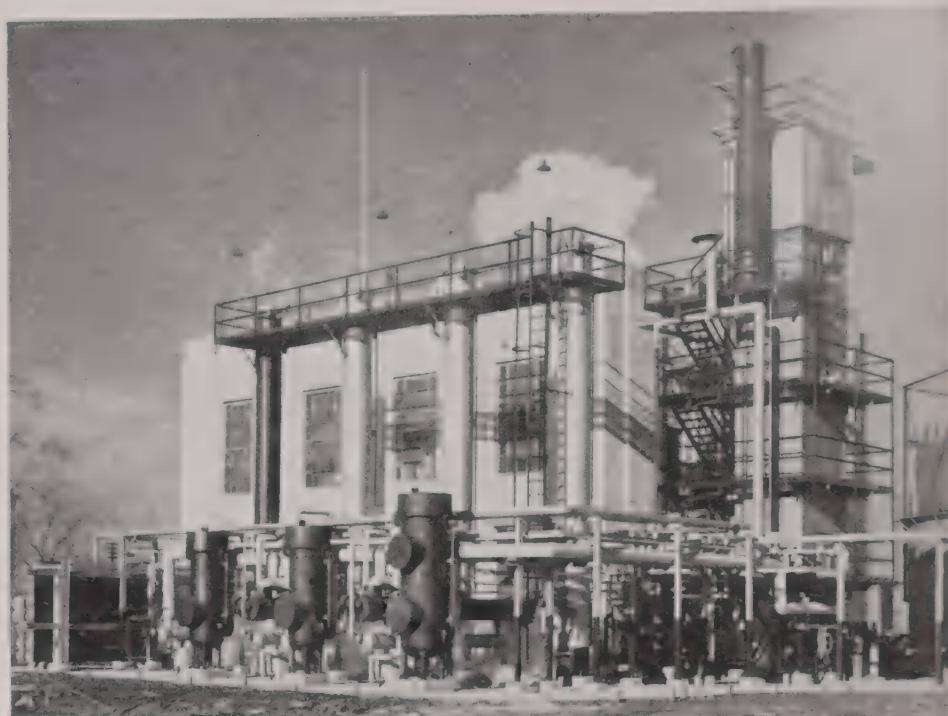
Fig. 114. Steam-hydrocarbon hydrogen plant. (Courtesy *The Girdler Corp.*).

are mixed and passed through furnace tubes containing a catalyst maintained at about 1500°F. A furnace of the type described by Shapleigh[72] is employed, which consists of one or more long alloy steel tubes supported vertically within refractory walls, and heated by burners supplied with natural or manufactured gas, fuel oil, or the same stock of propane as used for the feed. Flow of the mixture is downward, countercurrent to the hot flue gases. Space velocities of 600 volumes of hydrocarbon gas per hour per apparent unit volume of catalyst are attained.

Reaction takes place according to the following typical equation, which applies to propane:

$$C_3H_8 + 3\,H_2O \rightleftharpoons 3\,CO + 7\,H_2$$

[72] J. H. Shapleigh (to Hercules Powder Co.). Reissue 21,521 (1940) of U. S. Pat. 2,173,984 (1939).

A portion of the carbon monoxide formed undergoes further reaction (the so-called water gas shift reaction):

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$
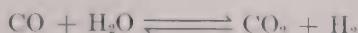
The mixture of hydrogen, carbon monoxide, and carbon dioxide issuing from the reforming furnace is mixed with steam to cool it to about 700°F., and the mixture is passed through a bed of another catalyst. Here the water gas shift reaction mentioned above converts 90–95% of the carbon monoxide to carbon dioxide and hydrogen. The exit gases are cooled to about 100°F., after which the carbon dioxide is removed by scrubbing with monoethanolamine solution as described in the succeeding section on hydrogen purification. The scrubbed gas contains about 1% of carbon monoxide, together with negligible amounts of methane, nitrogen, etc. Two additional stages of carbon monoxide conversion, identical with that described above, reduce the carbon monoxide content to *ca.* 0.001%. As an alternative to the third stage of conversion the last small proportion of carbon monoxide may be eliminated by methanation (see section on purification).

The water gas shift reaction, unlike the reforming reaction, is exothermic; hence there is some increase in temperature of the gases in the first carbon monoxide convertor. This is, however, not undesirable, as thereby the capacity of the unit is increased at some slight expense to the completeness of conversion. Heat exchangers may be installed to permit heat transfer to the cold inlet gases from the hot exit gases of each convertor following the first.

The following utilities and material requirements are given[71] for the hydrocarbon reforming process, per 1000 SCF of hydrogen produced:

Propane, process	2.75 gals.
or	
Natural gas	250 cu. ft.
Fuel equivalent to	350,000 B.t.u.
Steam	380 lbs.
Cooling water	1800 gals.
Electric power	2 kilowatt-hours
Chemicals, catalyst	2 cents

With each 1000 cubic feet of hydrogen, 300 cubic feet (35 pounds) of pure carbon dioxide are produced as a by-product.

The above figures apply to the manufacture of hydrogen of high purity, without the use of gas-to-gas heat exchangers.

In addition to the features enumerated above, a considerable advantage of the steam–hydrocarbon process is its great flexibility. If, for any reason, the hydrogenating plant becomes unable to take the full capacity of the hydrogen generating plant, the output of the latter can be readily reduced

by as much as 75% without significant decrease of operating economy.

Steam–hydrocarbon plants may be built with any desired capacity, but they are generally considered most economical in sizes of about 5000 cubic feet per hour or greater.

5. WATER GAS–CATALYTIC PROCESS[65,71]

The water gas–catalytic or steam–water gas process has long been used on a large scale for the manufacture of hydrogen for the synthesis of ammonia, methanol, etc., and is occasionally used in the fat hardening industry, although for making hydrogen of high purity it is now generally considered less economical and less satisfactory than the hydrocarbon reforming or steam-iron processes.

In the practice of this process water gas is prepared in the usual way, but with a minimum content of nitrogen and a maximum content of carbon monoxide and hydrogen. The water gas is then subjected to the water gas shift reaction and scrubbed free of carbon monoxide in much the same manner as described above for the latter stages of the hydrocarbon reforming process.

Utilities and materials requirements of this process, per 1000 SCF of hydrogen produced, have been listed[71] as follows:

Coke	42 lbs.
Steam	445 lbs.
Cooling water	1980 gals.
Electric power	3 kilowatt-hours
Chemicals, catalyst	2 cents

As a by-product, about 500 cubic feet or 58 pounds of carbon dioxide is produced per 1000 cubic feet of hydrogen.

By repeated conversion, carbon monoxide may be substantially eliminated from water gas catalytic hydrogen and most other impurities may be reduced to quite low levels. However, it is difficult to prepare hydrogen by this method with a nitrogen content below 1.5–2.0%.

6. HYDROGEN BY AMMONIA DISSOCIATION

Recently, it has been demonstrated that the mixture of 75% hydrogen and 25% nitrogen resulting from the catalytic dissociation of ammonia at elevated temperatures may be utilized effectively in the hydrogenation of certain stocks.[72a] The process is particularly attractive for processors who manufacture stearine or hydrogenate inedible fats on a small scale. For careful selective hydrogenation of edible stocks the use of

[72a] A. Van de Erve, W. A. Jacob, and R. W. Bates, *J. Am. Oil Chem. Soc.*, **25**, 60–63 (1948).

ammonia dissociation gas might be expected to offer difficulties in the way of maintaining a constant or controlled partial pressure of hydrogen in the hydrogenator. In any case, relatively high pressures are required to keep the partial pressure of hydrogen at a reasonable level without excessive purge losses.

7. HYDROGEN PURIFICATION

(a) *Removal of Carbon Dioxide*

Hydrogen purification will be considered apart from the individual processes for hydrogen production, since the same methods of purification are applicable to hydrogen made in different ways.

Carbon dioxide removal is usually effected by absorption in alkalies, in scrubbing towers of either the packed or tray and bubble cap type. In some plants, caustic soda is used as the alkali, the solution being merely circulated from a suitable reservoir through the tower until it is spent. Approximately 1.8 pounds of sodium hydroxide is required for the purification of 1000 cubic feet of hydrogen containing 1.0% of carbon dioxide or 0.9 pound for purifying hydrogen containing 0.5% carbon dioxide.

Alkali scrubbing also removes all but traces of hydrogen sulfide from the gas, but does not absorb organic sulfur compounds. Traces of carbon dioxide left in the hydrogen after scrubbing are unobjectionable, since this gas is not a catalyst poison, but serves merely as a diluent in the hydrogen.

Except possibly in very small installations the amine scrubbing system[70,71] is to be preferred, since spent amine solution may be easily and repeatedly regenerated for re-use. In commercial practice a 15–20% aqueous solution of monoethanolamine is generally employed. The reactions between amines and carbon dioxide and hydrogen sulfide are as follows:

$$2 RNH_2 + CO_2 + H_2O \rightleftharpoons (RNH_3)_2CO_3$$

$$(RNH_3)_2CO_3 + CO_2 + H_2O \rightleftharpoons 2 RNH_3HCO_3$$

$$2 RNH_2 + H_2S \rightleftharpoons (RNH_3)_2S$$

$$(RNH_3)_2S + H_2S \rightleftharpoons 2 RNH_3HS$$
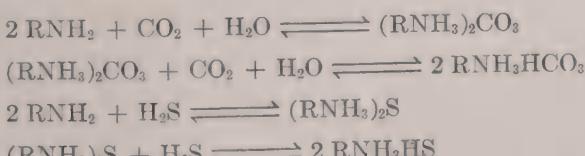
Each of the above reactions is reversible at moderately elevated temperatures, *i.e.*, slightly above the boiling point of water; consequently, the amines may be regenerated by heat.[73] In this respect they present a marked advantage over caustic soda or other inorganic alkalies, which

[73] R. R. Bottoms (to The Girdler Corp.), Reissue 18,958 (1933) of U. S. Pat. 1,783,901 (1930). L. B. Gregory and W. G. Scharmann, *Ind. Eng. Chem.*, *29*, 514–519 (1937). W. R. Wood and B. D. Storrs, *Proc. Am. Petroleum Inst. III*, *19*, 34–36 (1938).

require chemical treatment for recausticization or regeneration. Regeneration of the saturated amine is accomplished by passing it through a heat exchanger and then down a stripping column counter to a current of stripping steam generated in a reboiler in the base of the column.

The scrubbing towers are usually operated at atmospheric temperature and pressure. Some 2–4 cubic feet of carbon dioxide may be absorbed by each gallon of liquid circulated, and about 1 pound of steam is required for the regeneration of each gallon of solution.

In the hydrocarbon reforming process referred to above a single reservoir of amine solution is passed in series through the different scrubbing towers in countercurrent flow to the gas stream, so that it comes into contact with gas of progressively higher carbon dioxide concentration. One heater and stripping tower serves the entire system.

(b) Elimination of Carbon Monoxide

For carbon monoxide removal the system most in vogue at the present is essentially similar to the water gas–catalytic process described above, i.e., the carbon monoxide is reacted with steam at a high temperature over a catalyst to form carbon dioxide and hydrogen, after which the carbon dioxide is absorbed in an alkali.

Carbon monoxide removal must be very thorough, as hydrogen containing more than a few thousandths of one per cent of this gas will markedly poison the hydrogenation catalyst in hydrogenation conducted at low temperatures. In order to obtain purified hydrogen with the carbon monoxide concentration reduced to this order of magnitude, it is necessary to conduct the water gas–catalytic operation in two or more successive stages, removing the resulting carbon dioxide after each state. In some installations the bulk of the carbon monoxide is converted in one stage, and the small residue is then catalytically converted to methane, according to the scheme outlined below.

An alternative method for elimination of carbon monoxide is that of methanation. In this process the hydrogen is passed through a bed of nickel catalyst maintained at a temperature of 575–600°F. The carbon monoxide is converted to methane, which is inert toward hydrogenation catalysts, according to the following equation:

$$CO + 3\ H_2 = CH_4 + H_2O$$

One disadvantage of the methanation method of purification from carbon monoxide is that it produces another gas (methane) which cannot be easily removed from the hydrogen. Methane is not a poison for hydrogenation catalysts, but its accumulation in closed systems may be troublesome. Another disadvantage of the process is that it consumes hydrogen

equivalent to three times the volume of carbon monoxide reacted. In gas containing a relatively large amount of carbon monoxide the loss of hydrogen is not a negligible item of expense. On the other hand, it has the advantage of effecting a very complete removal of carbon monoxide. The combination of a one-stage water gas–catalytic purification followed by methanation thus offers the principal advantages of both systems. Complete removal of both hydrogen sulfide and organic sulfur compounds is prerequisite to successful operation of the methanation process; otherwise the methanation catalyst is rapidly poisoned and inactivated.

(c) Removal of Sulfur Compounds

Due to its extremely poisonous action toward hydrogenation catalysts, hydrogen sulfide must be completely removed from hydrogen which is to be used for fat hardening. The equipment often used for the removal of hydrogen sulfide from hydrogen is the same as that which has been used for many years in the manufactured gas industry, and consists of purifying boxes in which the gas is passed through a bed of iron oxide supported on wood shavings. After the purifying material is saturated with sulfur, it is revivified by simply being removed and exposed to the oxidizing influence of the atmosphere. The process of revivification is readily followed by observing the accompanying change in color of the material, from the black of iron sulfide to the reddish color of iron oxide. Since the purifying material may be re-used repeatedly, the chief expense of purification is in the labor required for charging and emptying the boxes.

As noted above, all but very slight traces of hydrogen sulfide are readily removable from hydrogen by scrubbing with caustic soda or ethanolamine solution.

Ordinary iron oxide treatment does not affect carbon disulfide, carbon oxysulfide, or other organic sulfur compounds in the hydrogen. These are readily absorbed, however, if the iron oxide is maintained at an elevated temperature, the following equation being representative of the reactions occurring:

$$CS_2 + 2 H_2O = CO_2 + 2 H_2S$$

At the temperatures ordinarly employed, the hydrogen sulfide is retained by the iron oxide, although if the reaction is carried out at a temperature above 300°C. (572°F.), it is said to remain in the hydrogen.

A suitable apparatus for organic sulfur removal consists of a small box equipped with trays bearing the iron oxide supported on mineral wool. The box is insulated, and in each tray are installed steam coils to maintain the temperature of the oxide in the neighborhood of 300°F. The temperature is not critical, however, and may be considerably higher or lower.

Hydrogen saturated with water vapor at ordinary temperatures carries a sufficient quantity of water for the above reaction, although it may be too dry if cooled to outside winter temperatures. Since the quantity of organic sulfur in the hydrogen does not usually exceed 0.5 grain of sulfur per 100 cubic feet, a single charge of oxide will suffice for the purification of a large volume of hydrogen, and operation of the process at a high temperature, in order to avoid retention of hydrogen sulfide by the catalyst, can hardly be considered worth while.

As noted previousy, bauxite and other metal oxides are effective catalysts for the conversion of organic sulfides to hydrogen sulfide, at *ca.* 700°F.

Sulfur compounds are troublesome only in processes which employ coke as a raw material; they constitute little or no problem in steam-hydrocarbon plants or in modern steam-iron plants using reformer reducing gas.

G. Hydrogenation in Practice

1. HYDROGENATION EQUIPMENT

Almost all of the oil hydrogenated commercially is processed in batch equipment. The failure of continuous equipment to become popular, during a period when the development and adoption of continuous processes have been the general rule in other oil processing operations, may be attributed to considerable mechanical difficulties in the way of achieving the close control and high selectivity of hydrogenation that is required by modern processors, and the diversity of hardening operations in most plants, which requires greater flexibility than is readily obtained in a continuous process.

In the design of a hydrogenation reactor the principal object is to obtain good mixing of the hydrogen and oil; mixing of the catalyst–oil mass is of minor importance. Hence an efficient hydrogenator is essentially an efficient and easily controlled gas absorber. In the early days of the hydrogenation process, favor was divided between the so-called Wilbuschewitsch system, in which the oil was sprayed into an atmosphere of hydrogen, and the Normann system, in which hydrogen is bubbled into a body of the oil. In the United States, at least, the relatively elaborate Wilbuschewitsch system is now seldom used, and modern development of the Normann system has been in the direction of simplifying rather than elaborating the apparatus.

The hydrogenation plants now operating commercially in this country are essentially divided between "recirculation" systems in which agitation and dispersion of hydrogen within the oil are achieved by contin-

uously recycling hydrogen in large volumes through the reactor, and the newer "dead-end" systems in which the reactor is supplied only with as much hydrogen as is absorbed, and dispersion of the hydrogen is assisted by mechanical agitation.

(a) Batch Equipment. Recirculation System

The general design and layout of a plant for hydrogenation by the recirculation of hydrogen is shown in Figure 115. The reactor proper is a tall cylindrical vessel, usually built to hold 20,000–40,000 pounds of oil,
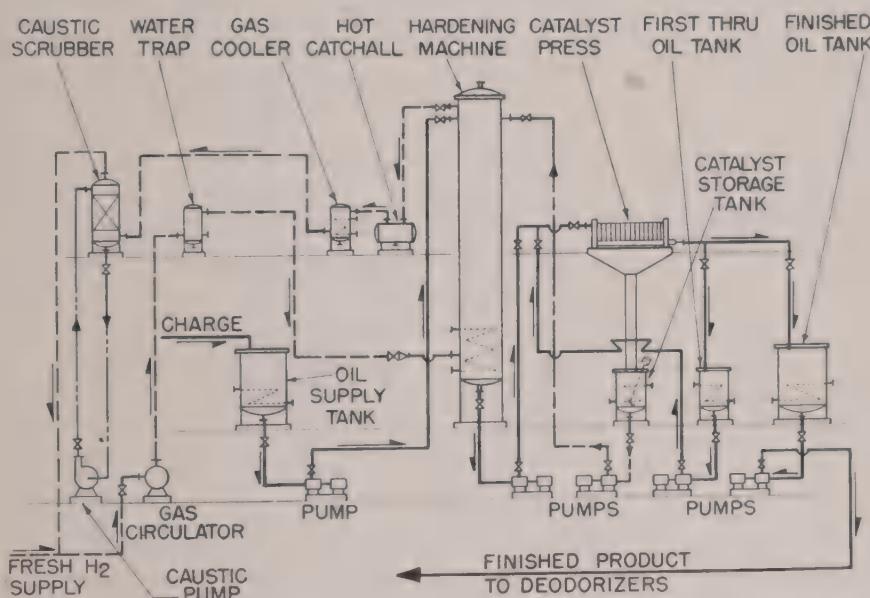
Fig. 115. Hydrogenation plant employing hydrogen re-circulation (courtesy *The Foster Wheeler Corp.*).

containing heating coils and a distribution device in the bottom for breaking the injected hydrogen up into many small streams. A blower or compressor is provided, of large capacity, which continuously withdraws hydrogen from the headspace of the reactor, forces it through a purification train, and sparges it back into the oil. Undue build-up of nitrogen or other nonremovable impurities in the hydrogen is avoided by intermittent venting to the atmosphere. With steam–hydrocarbon hydrogen of good quality, venting of 3–4% of the total hydrogen is adequate.[73a] Although hydrogen is sometimes supplied to a recirculating reactor from high-pressure storage tanks, it is more usual to store the hydrogen in a large low-pres-

[73a] F. B. White and S. Faulkner. Abstracts of Papers, 23rd Fall Meeting, American Oil Chemists' Society, Chicago, 1949.

sure holder. The recirculating blower may be designed to build up a moderate pressure upon the reactor, but more commonly the reaction is carried out at a pressure only slightly above that of the atmosphere. There are considerable differences of opinion as to the benefits of the hydrogen purification train, and with respect to this portion of the apparatus there is much variation in design. The earlier plants subjected the recirculating gas to water washing, caustic scrubbing, and, in some cases, even to contact with activated carbon. In using the relatively pure hydrogen supplied by modern electrolytic, steam–hydrocarbon, or steam–iron plants, there appears to be some doubt that there is any real advantage in elaborate purification, and some processors employing this system omit all steps except water washing, and retain this step only as a covenient means of cooling the exit hydrogen before it reaches the recirculating blower.

In the operation of the recirculating system, the reactor is almost al-
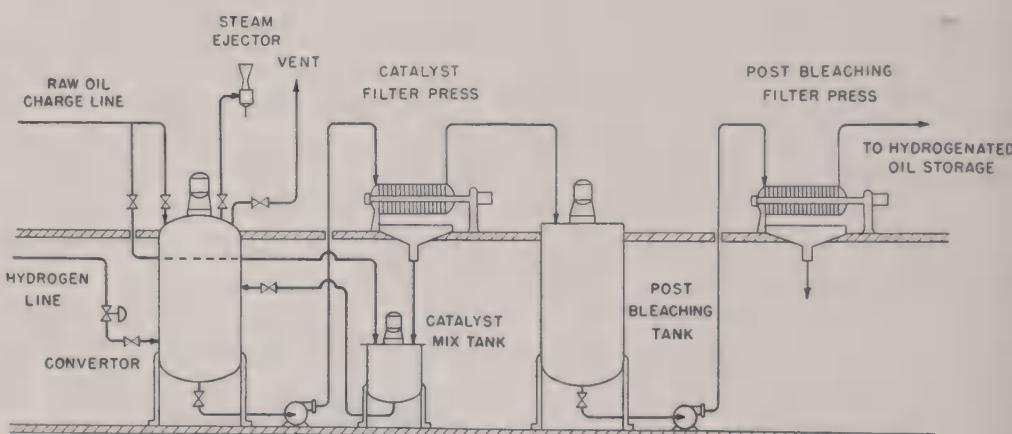
Fig. 116. Hydrogenation plant, dead-end type (courtesy *The Girdler Corp.*).

ways kept filled with hydrogen under holder pressure at all times, *i.e.*, it floats upon the low-pressure holder except when hydrogenation is actually in progress. When the catalyst is added with the oil charge, as is usual, hydrogenation takes place during the heating period and thereafter as long as is required to reduce the oil to the desired iodine value; water is admitted to the cooling coils to carry away heat of reaction and maintain the temperature within proper limits. At the conclusion of the reaction, hydrogenation is stopped by shutting down the blower, and the finished charge is pumped out through an external cooler to a filter press where the catalyst is removed, and thence to "post bleaching" and to storage.

Practice varies in the handling of the catalyst in both recirculating and dead-end systems. A small catalyst mix tank is usually provided for receiving the catalyst press cake and resuspending it in oil for re-use, or

for melting and slurrying fresh catalyst. In some plants, the identity of each charge of catalyst is preserved as it is used in successive runs. In others, the catalyst slurry from each finished batch of oil is pumped into holding tanks and mixed with other similar catalyst, with different tanks being provided for "first-run" catalyst, "second-run" catalyst, etc.

(b) Batch Equipment. Dead-End System

Modern dead-end hydrogenators, or convertors, as they are more commonly called, are closed, vertical cylindrical steel vessels, of about 10,-000–40,000 pounds capacity, designed for full vacuum and 100–150 pounds working pressure. Coils within the vessel are provided to take either steam for heating, or cooling water. A vertical shaft carrying a motor-driven agitator is inserted through a stuffing box or seal in the top head. As they require less headspace above the oil charge, they are generally somewhat shorter in relation to their diameter than the reactors used with the recirculating system.

Only special agitators, designed to give efficient hydrogen dispersion, are satisfactory for dead-end convertors. The agitator that is most widely used at the present (Fig. 117) has two or more turbine-type impellers of a special shrouded design, with the top impeller being placed relatively near the surface of the oil and provided with a suction sleeve that projects into the headspace and induces hydrogen from the headspace back into the oil. A newer, but highly efficient agitator,[73b] employs impellers consisting of a series of flat paddles set vertically around the periphery of a flat horizontal disc. Vertical banks of tubes around the inner wall of the vessel serve the double purpose of heating or cooling the charge and providing baffles to limit swirling of the oil and improve hydrogen dispersion. In convertors equipped with this type of agitator, induction of hydrogen from the headspace occurs through a vortex extending down to the top impeller.

An important accessory of the dead-end system is a steam ejector system capable of quickly evacuating the empty convertor and maintaining a vacuum of about 28 inches. Hydrogen is supplied to the convertor from high-pressure storage tanks, through a reducing valve set at a constant operating pressure, and is admitted to the convertor only when hydrogenation is actually in progress.

In operation, the dead-end convertor is kept under vacuum while the charge of oil and catalyst is being pumped in, and also during the heating period, the object of this being to deaerate and dry the oil before it reaches a high temperature, and also to prevent reaction during heating, and thus avoid hydrogenation over a range of temperatures. When steam

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[73b] See C. J. O'Boyle, *Ind. Eng. Chem.*, *42*, 1705–1714 (1950).

in the heating coils has carried the batch to the required operating temperature, the vacuum line is closed and hydrogen is admitted to the vessel and allowed to build up to the pressure desired. At the end of the hydro-
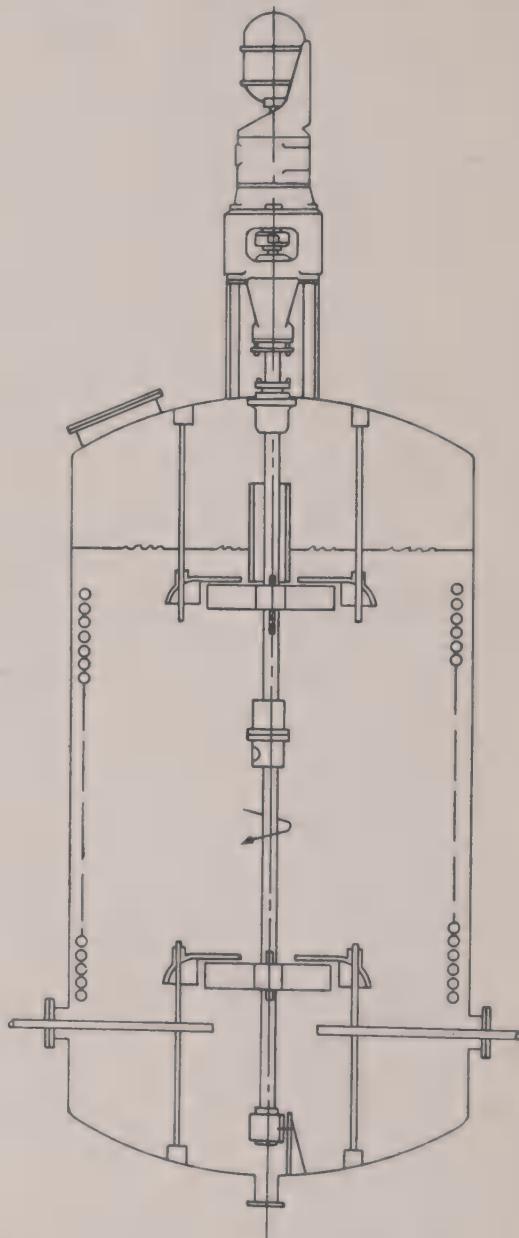
Fig. 117. Dead-end convertor with shrouded turbine-type agitator and suction sleeve for internal circulation of hydrogen (courtesy *The Turbo-Mixer Corp.*).

genation period, the flow of hydrogen is stopped, the hydrogen in the headspace, with accumulated impurities, is blown off to the atmosphere,

vacuum is again placed on the vessel, and the charge is cooled to about 160–190°F. by water in the coils, with the agitator running. Then, vacuum is broken, and the batch is pumped out through a filter press, as from any open vessel, with the first cloudy oil through the press being diverted back to the convertor. A vent line to the atmosphere should be installed between double block valves in the hydrogen line to the convertor, and this should be opened except when the convertor is under pressure, to prevent accidental leakage of hydrogen into the vessel.

Some processors operate mechanically agitated convertors in such a manner as to combine certain typical features of the dead-end and the recirculating systems, as described above. For example, external oil coolers are used, the convertors are not always evacuated, and a small flow of hydrogen is sometimes bled from the convertor headspace back to the hydrogen plant for recompression, or a small blower is installed to give limited external hydrogen recirculation.

Hydrogen losses in the operation of the dead-end system depend upon the amount of hydrogen discharged from the headspace of the convertor at the conclusion of the run, in relation to the amount absorbed by the oil, and upon the care exercised in preventing hydrogen leakage. In well-designed and well-operated plants using pure hydrogen and producing shortening and margarine oil stocks from cottonseed and soybean oil, they do not exceed 3–5% of the hydrogen reacted.

The claimed advantages of dead-end hydrogenation with evacuation of the convertor, in comparison with hydrogenation by gas recirculation, are: (a) prevention of oxidation and hydrolysis of the oil, through de-aeration and dehydration of the charge; (b) more positive control of the reaction and consequent improved product uniformity (the entire reaction is carried out at a definite and constant temperature, and the amount of hydrogen absorbed by the oil is easily ascertained from the pressure drop on the hydrogen supply tank); (c) greater latitude in selectivity and decreased dependence upon the temperature as a factor determining selectivity (as the operating pressure can be widely varied); and (d) simpler, less expensive, and more easily maintained equipment.

Well-designed dead-end and recirculating systems are about equally efficient with respect to the speed of the reaction. Operated at 350°F. and 0–5 pounds pressure with 0.05–0.10% of active nickel and pure hydrogen, either will, for example, reduce the iodine value of cottonseed oil from 108 to 70 in about 40–60 minutes. There appear to be no inherent differences in the composition of products of the two systems, except in relation to the temperature and pressure limitations mentioned above.

(c) Continuous Equipment

The continuous hydrogenation process developed by Bolton and Lush[74] employs a catalyst consisting of nickel turnings enclosed in a cylindrical cage of metal screen. The cages are encased in cylinders, through which the oil is pumped continuously, in an atmosphere of hydrogen. The surface of the catalyst is rendered catalytically active by first forming upon it a coating of oxide by "anodic oxidation," and then reducing the oxide back to the metal at a relatively low temperature. In the process of anodic oxidation, the cage and its contents are made the anode in an electrolytic bath employing sodium carbonate as an electrolyte. Passage of a direct current for a suitable period, followed by thorough washing of the catalyst, places the latter in condition to be reduced to an active form. After the catalyst has become inactivated in use it is restored to its original activity by extraction with a solvent, and repeated anodic oxidation and reduction.

Two methods are described for operation of the Bolton-Lush apparatus. It may be operated by the "drip" method, in which the oil is allowed to drip down the catalyst mass, without flooding of the latter, or by the "overflow" method, in which the catalyst chamber is filled with oil at all times. The drip method yields a product very low in iso-oleic acid, but nonselectively hydrogenated. In operation by the overflow method, somewhat greater selectivity is obtained, but the production of iso-oleic acid is very high.

An active catalyst mass, consisting of 10% metal and 90% voids, is said to be capable of hydrogenating cottonseed oil to an iodine value of 50 at a rate equivalent to its own weight each hour.

Continuous hydrogenation systems employing a powder catalyst have been devised, but these have been used commercially only to a very limited extent.

A recent series of patents issued to Mills and associates[16a,74a] describes a continuous hydrogenation apparatus which combines intensive agitation with the use of relatively high pressures to achieve extremely rapid hydrogenation. In a typical example given in the patent specifications cottonseed oil was hydrogenated to an iodine value of 74.5 with a residence time in the reactor of only 4.8 minutes. A powder catalyst equivalent to 0.10% nickel was used, and hydrogenation was conducted at 110–112°C. under 150 pounds per square inch gage pressure.

[74] E. R. Bolton, J. Soc. Chem. Ind., 46, 444–446T (1927). E. J. Lush, ibid., 42. 219–225T (1923). L. H. Manderstam, Oil & Soap, 16, 166–172 (1939).
[74a] V. Mills (to Procter & Gamble Co.), U. S. Pat. 2,520,425 (1950).

2. Characteristics of Hydrogenated Oils

(a) Effect of Hydrogenation on Characteristics Other Than Melting Point or Consistency

The characteristic of oils most directly affected by hydrogenation is the iodine value, which decreases in direct proportion to the amount of hydrogen absorbed. Characteristics which do not depend upon the unsaturation of the oil, such as the saponification value, hydroxyl value, Reichert-Meissl value, content of unsaponifiable matter, etc., are substantially unchanged by hydrogenation.

Certain nonglyceride constituents of fats and oils are reduced during hydrogenation, including carotenoid pigments and probably also unsaturated hydrocarbons. The hydrogenation of carotenoids usually causes a marked reduction in the color of vegetable oils. Unbleached palm oil, which is naturally of a very deep orange-red color, is no darker than other vegetable oils after it is hydrogenated. The color of bleached cottonseed oil as measured on the Lovibond scale is often decreased as much as 50%, and that of soybean oil is usually reduced even more.

Concurrently with the reduction of carotenoids the vitamin A activity of oils is destroyed. However, by operating at low temperatures (e.g., 40–60°C.) and high pressures (200–1000 lbs. per square inch) it is claimed[75] that fish oils can be partially hydrogenated without material loss of vitamin potency.

Ordinarily, the free fatty acid content of dry oils is not measurably affected by hydrogenation. However, with certain catalysts, and particularly with the nickel sulfate catalyst described previously, prolonged hydrogenation at a high temperature may increase the free fatty acid content by as much as 0.1–0.3%.

Hydrogenation, if carried at all far, will destroy the natural flavor and odor of any oil or fat, producing in its stead a distinctive, rather unpleasant "hydrogenation odor," which must be removed from edible fats by steam deodorization. This odor is attributed by Mielck[76] to ethers of higher and lower alcohols, possibly in conjunction with acetyl carbinol resulting from hydrogenation of the diglycerides that are present in at least traces in all oils.

The stability of oils, as measured by accelerated oxidation tests, is progressively increased as the oils are hydrogenated. The relationship between stability and the composition of hydrogenated oils is discussed in detail in connection with shortening manufacture (Chapter VII).

[75] J. G. Blaso (to Natural Vitamins Corp.), U. S. Pats. 2,307,756 and 2,311,633 (1943). D. J. Hennessy (to Vitamoil Lab., Inc.), U. S. Pat. 2,321,913 (1943). H. I. Waterman and J. A. van Dijk, U. S. Pat. 2,143,587 (1939).
[76] H. Mielck, Seifensieder-Ztg., 57, 241–242 (1930).

Hydrogenation reduces the refractive index of oils, the relationship between iodine value and refractive index depending largely upon the average molecular weight of the glycerides. This relationship is very nearly the same for many fats and oils (Fig. 118), although rapeseed and other erucic acid oils, which are high in molecular weight, and coconut oil and other lauric acid oils, which are low, deviate quite markedly from the average. The correlation between iodine value and refractive index
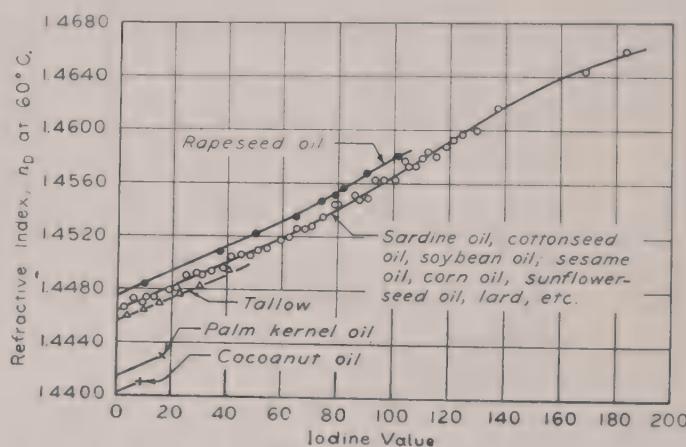
Fig. 118.   Iodine value *vs.* refractive index for various hydrogenated oils.
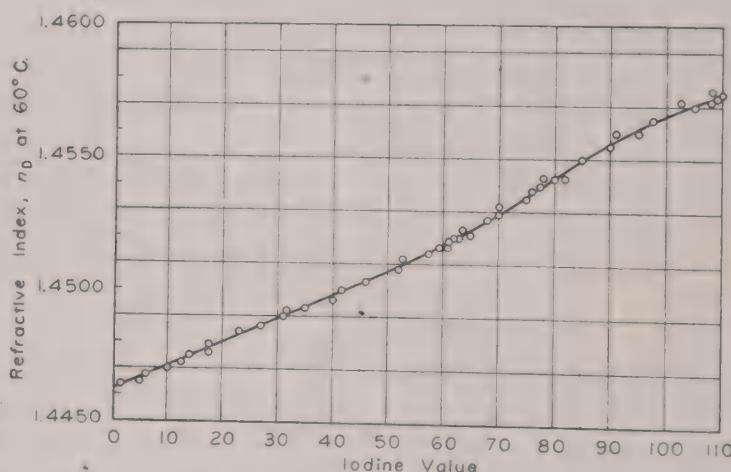
Fig. 119.   Iodine value–refractive index relationship in hydrogenated cottonseed oil.

is not precise for any given variety of oil, but the refractive index will generally serve to indicate the iodine value of a hydrogenated oil within one or two units (see Fig. 119) or even less in the case of a single lot of oil hydrogenated under a fixed set of conditions. Since refractive index measurements may be easily and quickly made, they are often used as means of controlling the hydrogenation. An actual iodine value by the

rapid method of Hoffman and Green[77] can be determined almost as quickly, and it of course gives a closer indication of the progress of hydrogenation.

(b) Effect of Hydrogenation on Melting Point and Consistency

During the first stages of hydrogenation, the consistency of an oil, and its characteristics related to consistency, such as melting point, softening
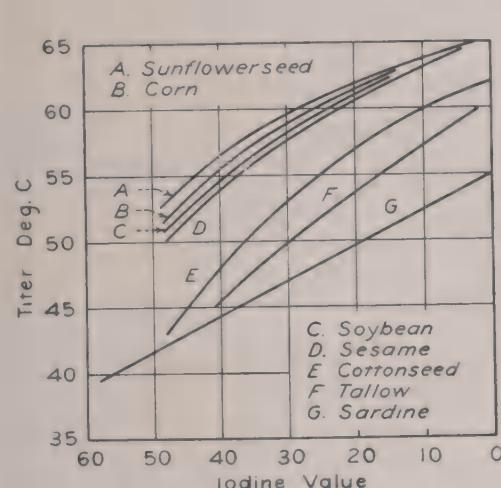
Fig. 120. Iodine value *vs.* titer for various hydrogenated oils.
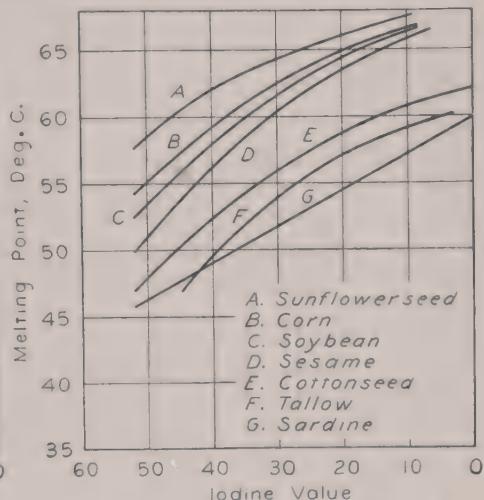
Fig. 121. Iodine value *vs.* melting point (clear point in closed capillary tube) for various hydrogenated oils.
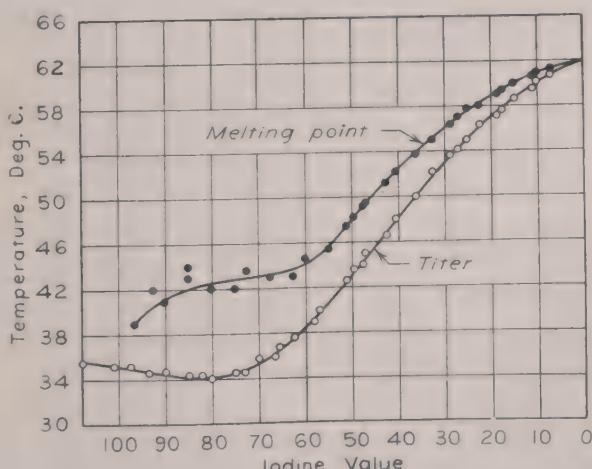
Fig. 122. Iodine value *vs.* titer and melting point (clear point in closed capillary tube) of hydrogenated cottonseed oil. (Catalyst used was relatively nonselective, and samples were high in both saturated acids and iso-oleic acids at the higher iodine values.)

[77] H. D. Hoffman and C. E. Green, *Oil & Soap, 16*, 236–238 (1939).

point, congeal point, etc., depend a great deal upon the conditions of hydrogenation and the characteristics of the catalyst. For example, if the consistency is measured by the micropenetration method outlined by Feuge and Bailey,[78] the micropenetration at 22.5°C. (72.5°F.) of cottonseed oil hydrogenated to an iodine value of 65 may be as low as about 25 or as high as about 125, according to the amounts of saturated and iso-oleic acids in the sample. The melting point varies according to the saturated fatty acid content, and hence is dependent upon the selectivity of the reaction. At an iodine value of 67, Williams[79] recorded melting points for hydrogenated cottonseed oil varying from 35.9° to 53.1°C., as the temperature of hydrogenation was decreased from 180° to 130°C.
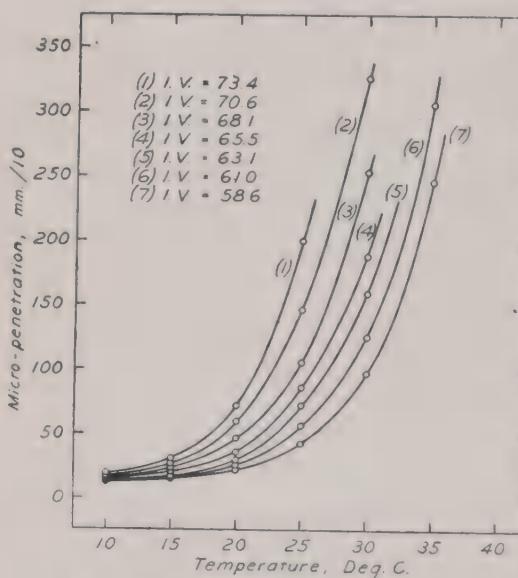
Fig. 123. Typical micropenetration curves of cottonseed oil hydrogenated to different degrees.[78]
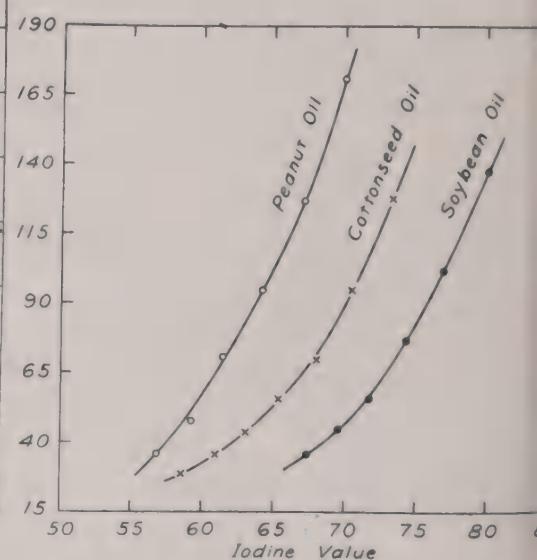
Fig. 124. Typical variations in the consistency of different oils with hydrogenation. Micropenetrations at 22.5°C. (mm./10) vs. iodine value of the oils.[78]

In the later stages of hydrogenation, the percentage of saturated acids in the oil becomes a function simply of the iodine value of the oil, and the percentage of iso-oleic acid is not greatly different under different conditions of hydrogenation, so that the melting point, etc. are quite predictable from the iodine value. Typical curves of iodine values vs. melting point and titer, for various highly hydrogenated oils, are reproduced in Figures 120 and 121. The titer of hydrogenated cottonseed oil exhibits the peculiarity of passing through a minimum at an iodine value between 80 and 85 (Fig. 122).

[78] R. O. Feuge and A. E. Bailey, Oil & Soap, 21, 78–84 (1944).
[79] K. A. Williams, J. Soc. Chem. Ind., 46, 448–449T (1927).
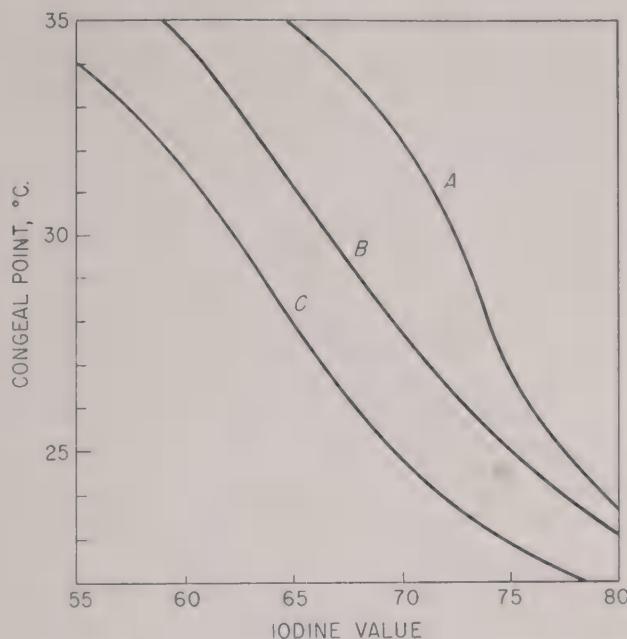
Fig. 125. Iodine value *vs.* congeal point of hydrogenated oils: (*A*) soybean oil (data of Harrington *et al.*[80]), (*B*) cottonseed oil with a moderately selective catalyst, and (*C*) cottonseed oil with a very highly selective catalyst.
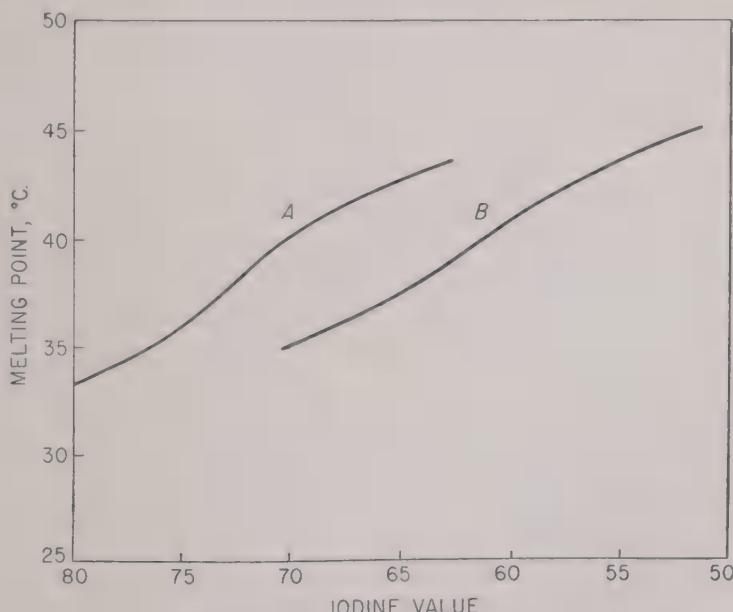
Fig. 126. Iodine value *vs.* Wiley melting point of: (*A*) selectively hydrogenated soybean oil, and (*B*) selectively hydrogenated cottonseed oil.

The typical alteration of consistency with hydrogenation is illustrated in the case of different oils in the micropenetration curves of Figs. 123–4.

Typical iodine value–congeal point curves are shown in Figure 125. Curves *B* and *C* of this figure serve only to illustrate differences that may be obtained in hydrogenating an oil under fixed hydrogenation conditions with two different commercial catalysts. Much greater differences occur when the conditions of hydrogenation are likewise varied. Typical curves showing the iodine value–melting point relationship in the shortening or margarine stock range are reproduced in Figure 126.

The lack of selectivity with respect to the hydrogenation of glycerides, quite as much as the equally unavoidable formation of iso acids, renders it impossible to produce hydrogenated fats or oils which are equivalent to some of the natural fats. As shown by the researches of Hilditch and co-workers, the saturated fatty acids in vegetable oils tend to be associated in the glyceride molecules with a maximum proportion of unsaturated fatty acids, so that there is a minimum content of highly saturated glycerides. Consequently, these oils tend to be softer in consistency and lower in melting point than it is possible to make hydrogenated oils of the same iodine value. Olive oil, for example, has an iodine value in the neighborhood of 80, but remains liquid down to quite low temperatures. Soybean oil hydrogenated to this iodine value is lardlike in consistency at ordinary atmospheric temperature. Animal fats, on the other hand, have their saturated fatty acids less evenly distributed, and hence can be approached quite closely in consistency by hydrogenated oils of equivalent iodine value. Lard substitutes can be prepared by the hydrogenation of vegetable oils with iodine values in the same range as those of lard, *i.e.*, about 60 to 70.

If two oils of different iodine value are to be hydrogenated to yield products of the same consistency, the more unsaturated oil cannot be hydrogenated to as low an iodine value as the less unsaturated oil. Or stated somewhat differently, the further an oil is hydrogenated, the greater is its deviation in character from natural oils. Thus, for example, a shortening of the all-hydrogenated type prepared from peanut oil may have an iodine value of 55 or lower, whereas similar shortenings made from cottonseed oil usually have iodine values greater than 60, and it is hardly possible to make such a shortening from soybean oil with an iodine value below about 70.

(c) *Analytical Methods for Hydrogenation Control*

Even though different batches of oil are hydrogenated under uniform conditions to precisely the same iodine value, it will be found that slight

variations will inevitably occur in their composition and characteristics. Hence it is necessary to control the hydrogenation of edible oils according to their physical characteristics, rather than strictly according to the amount of hydrogen absorbed. In practice, it is customary to adjust the conditions of hydrogenation so as to obtain the proper balance between the formation of saturated and iso-oleic acids, and then carry hydrogenation of the oil far enough to bring all batches to a uniform consistency at ordinary atmospheric temperatures, *i.e.*, at some temperature in the range of about 70–75°F.

The problem of hydrogenation control is less difficult if more than one hydrogenated stock is blended to produce the product in question, and if a number of convertor batches can be blended in making up each lot. sistencies is not permissible to the same degree as in handling shortening stocks, inasmuch as the former (in the United States) are usually not blends, but consist of a single stock hydrogenated to the proper consistency. Furthermore, the blending of different batches to smooth out inconsistencies is not permissible to the same degree as in handling shortening stocks. In the manufacture of some stocks, including the most carefully prepared margarine oils, it is almost essential to interrupt hydrogenation at some point short of the end point, and check the consistency of the oil by analysis, before finishing the batch.

However, after the proper end point is established for a given lot of oil and catalyst, the hydrogenation of subsequent batches can usually be satisfactorily controlled by hydrogen absorption or refractive index alone, inasmuch as irregularities can usually be traced to variations in the oil or the catalyst.

Of the various analytical methods for judging the consistency of hydrogenated fats, the setting point or congeal point is perhaps the most widely used. The details of this method have never become standardized, and vary from one laboratory to another, with corresponding minor variations in the congeal point itself. One variation of the method is as follows:

Approximately 100 ml. of fat is placed in a 250-ml. tall-form electrolytic beaker, and the fat is placed in a 5°C. water bath and rapidly stirred with a titer thermometer until it begins to cloud. The sample is then alternately stirred and removed from the bath for observation until it is sufficiently cloudy to make the bulb of the thermometer barely visible when the latter is held in the center of the beaker. The beaker is then quickly dried and placed in a 20°C. air bath, with the thermometer bulb suspended quietly in the center of the fat mass. Readings of the thermometer are taken at two-minute intervals, and the highest reading is recorded as the setting point or congeal point.

Determination of the congeal point is somewhat time consuming, and as an alternative, some laboratories do not carry the solidification to a point of thermal equilibrium, but cool a molten fat sample under carefully controlled conditions until a "cloud point," corresponding to a standard degree of turbidity is reached, with the latter being noted either visually or photoelectrically.[79a] Harrington and co-workers[80] have described a method depending upon the development of an arbitrary viscosity as the fat is similarly cooled and partially crystallized.

Actually, congeal points, cloud points, etc., are not direct measures of the consistency of the fat, but rather are characteristics which may be correlated with the consistency at 70–75°F., provided that the selectivity of hydrogenation is approximately known. There may be considerable variation in the congeal point, etc., without variation in the consistency, if the selectivity of hydrogenation is allowed to change. A very selectively hydrogenated margarine oil, for example, may have a congeal point as low as 27°C. and be no softer at 70–75°F. than a nonselectively hydrogenated shortening with a congeal point of 32–33°C.

The quick micropenetration method described by Feuge and Bailey[78] is not much more time consuming than the congeal point, and has the great advantage of being an actual measure of consistency, and hence of serving to evaluate this property independently of the selectivity of hydrogenation. It requires special apparatus, however, and somewhat more careful manipulation than the other methods referred to above.

Hard oil, stearine, or "flakes" is usually hydrogenated to a definite titer (or clear capillary tube melting point). In highly hydrogenated products the relationship between titer and melting point is dependable; hence hydrogenation may be satisfactory controlled by the refractive index or iodine value.

In following closely the course of hydrogenation by any of the preceding methods the best procedure is to maintain a running plot of hydrogenation time against iodine value as a general guide to the course of reaction. During the first stages this plot may be made quite roughly, with iodine values being estimated from refractometer readings or from the drop in pressure of the hydrogen tank supplying the convertor. As the desired degree of reaction is approached the exact position of the curve should be fixed by making a quick iodine value determination.[77] At the same time the quick micropenetration, congeal point, or other critical characteristic should be determined. Then from the relationship between the two (by consulting families of typical curves established from previous runs) it is easily possible to determine by extrapolation how much

[79a] See W. H. Shearon, Jr., H. E. Seestrom, and J. P. Hughes, *Ind. Eng. Chem.*, 42, 1266–1278 (1950).
[80] B. S. Harrington, F. B. Crist, A. A. Kiess, and W. A. Jacob, *Oil & Soap*, 22, 29–30 (1945).

farther the iodine value should be dropped to bring the critical character-
istic to the desired value. The proper drop in iodine value can be brought
about by extending the hydrogenation time according to indications of the
time–iodine value curve or by continuing the reaction until the required
amount of hydrogen (calculated from gage readings) is absorbed.

Naturally, the more closely the end of the reaction is approached before
a check is made, *i.e.*, the less extrapolation is required, the more precisely
will the end point be determined. In very careful work it may be necessary
to make repeated checks on more than one sample. If the end point is
thus aproached very cautiously, or in any case if reaction is relatively
rapid, the reaction will have to be stopped while the oil samples are being
analyzed.

For control in the blending of hydrogenated stocks to product shorten-
ing, congeal (or cloud) point and melting point determinations are often
relied upon, although penetrometric or dilatometric methods are to be
preferred.

3. Hydrogenation of Hard Oils or Stearine

Hydrogenated stearines, or hard oils, are principally manufactured for
use in making blended type shortenings, for imparting high-temperature
body to all-hydrogenated shortenings, or for stiffening soft lards. They
may also be desired as raw materials for the production of stearic acid,
however, or for a variety of other purposes. The terms "vegetable stea-
rine" and "animal stearine" are applied respectively to vegetable and
animal oils or fats which have been hydrogenated to a brittle consistency
and an iodine value usually less than about 20, and often in the range
5–10. The stiffening capacity of a hard oil is very closely measured by its
titer. Vegetable stearine was originally prepared as a substitute for oleo-
stearine, which has a titer of about 50°C., and must be mixed with cotton-
seed oil in the ratio of about 20 parts to 80 to produce a shortening of the
proper consistency. It is now customary to hydrogenate vegetable oils to
a titer of 58° or above; not more than 10–15% of such a hard oil is re-
quired in a blended shortening.

Some oils can be hardened to considerably higher titers than others
(Fig. 120); soybean oil, sunflower oil, corn oil, or sesame oil may be
hydrogenated to a titer as high as 65°C. It is not convenient to use these
oils in a highly hardened form for blended shortening manufacture, how-
ever, because of their excessive tendency to solidify in low-melting, un-
stable polymorphic forms if reduced to a low iodine value. This causes
trouble in the solidification and subsequent handling of the shortening.
The tendency toward polymorphism (as well as the high titers) is un-
doubtedly a result of the predominance of C_{18} acids in these oils, which
causes the completely hardened product to consist largely of tristearin.

Cottonseed oil, palm oil, lard, tallow, or fish oils contain a sufficient proportion of acids higher and lower than C_{18} to insure that little tristearin will be formed, and give little trouble from polymorphic effects.

The hydrogenation of stearine is the least critical of all hydrogenation operations; such considerations as selectivity and iso-oleic acid suppression are naturally unimportant in the manufacture of this product. If a catalyst is to be used only for hard oil production, it may be selected purely on the basis of its activity. In order to make the reaction as rapid as possible, the highest possible pressure is usually used, and the temperature is often allowed to rise as high as 400–425°F. At high temperatures and pressures, it may be that the rate at which hydrogenation can be conducted will depend upon the capacity of the cooling coils in the hydrogenator for carrying away the heat of the reaction, which is strongly exothermic (see page 687). Ordinarily about 3 to 4 hours will be required to reduce cottonseed oil to an iodine value of 10 and a titer of 60°C., at a pressure of 60 pounds gage, a maximum temperature of 400°F., and a catalyst concentration equivalent to 0.03–0.04% of fresh, active nickel. If only new catalyst is used, the best results will be obtained by reserving a portion of the catalyst to be added toward the end of the hydrogenation, e.g., 0.02–0.04% may be added to the hydrogenator at the beginning of the run, and 0.01–0.02% may be added after the iodine value is reduced to about 30 or 40. Catalyst which has been partially inactivated in the manufacture of other products may be used to good advantage in making hard oil, although some catalysts are inclined to produce excessive amounts of free fatty acids in the oil, if so used in extremely high concentrations.

4. HYDROGENATION OF SHORTENING STOCKS

In the shortening trade in the United States so-called all-hydrogenated shortenings constitute a distinctive class of high-grade products, which are manufactured to rigid standards of color, free fatty acid content, flavor and odor, stability, and consistency. They are hydrogenated in such a manner as to obtain the lowest iodine value and the highest stability that is consistent with the proper consistency. With care, the proper consistency at 70–75°F., together with reasonably good body at higher and lower temperatures, can be obtained with iodine values as low as 60–65 in the case of shortening made exclusively from cottonseed oil, and 70–75 in all-soybean oil products. Comparable shortenings made from peanut oil alone have not appeared upon the market in quantity, but presumably they would have iodine values slightly lower than those of cottonseed oil shortenings.

Iodine values such as those listed above are obtained by so adjusting the hydrogenation conditions as to minimize the formation of iso-oleic

acid and at the same time obtain reasonably good selectivity and prevent the formation of excessive amounts of saturated acids. This adjustment is a somewhat delicate matter, since conditions, leading to high selectivity and low iso-oleic acid formation are to some extent mutually exclusive.

Conditions suitable for the hydrogenation of all-hydrogenated shortenings can hardly be stated categorically, due to differences in agitation in different hydrogenators, variations in catalyst activity, and the varying

TABLE 122

ALL-HYDROGENATED SHORTENINGS MADE FROM COTTONSEED OIL: ANALYSES OF TYPICAL PRODUCTS MADE UNDER DIFFERENT HYDROGENATION CONDITIONS

| | Sample number | | | |
| | | | 3[a] | |
Conditions and analyses	1	2	First stage	Second stage
Hydrogenation conditions:				
Temperature, °F.	218	275	165	250
Pressure, lbs./sq. in. gage	50	50	50	50
Catalyst, % nickel	0.07	0.10	0.07	Same
Hydrogenation time, min.	175	63	130	25
Iodine value at end of hydrogenation period	63.8	62.8	75	62.5
Composition of fatty acids, finished shortening:				
Saturated, %	32.7	28.8	33.0	
Iso-oleic, %	10.2	14.0	8.1	
Oleic, %	50.7	55.4	53.9	
Linoleic, %	6.4	1.8	5.0	
Micropenetrations of finished shortening, mm./10, at:				
45°F.	15	13	15	
70°F.	55	55	55	
85°F.	165	180	130	
98°F.	340	Almost melted	320	
Stability, by Swift method, hrs.	75	200	98	

[a] Hydrogenation conducted in two stages.

degrees of selectivity that are required. However, in general it may be said that these conditions will be about as follows: pressure, 10 to 60 pounds, gage; temperature, 200° to 300°F., and catalyst concentration. 0.05 to 0.10% nickel. Some hydrogenators prefer to conduct the operation in successive steps at two different temperatures, employing a low temperature in the first stage to minimize iso-oleic acid formation and a high temperature in the second stage to reduce the percentage of linoleic acid.

All-hydrogenated shortenings of the biscuit and cracker type are pre-

pared similarly to regular all-hydrogenated shortenings, except that the hydrogenation is conducted more selectively. These shortenings have insufficient saturated acids to give them a good high temperature body, but they are very low in linoleic acid and correspondingly high in stability.

The operating and analytical data contained in Table 122 may be considered more or less representative of good practice with an active, fresh, catalyst, hydrogen free from catalyst poisons, and hydrogenation equipment employing efficient agitation. Of the samples in this table, *1* and *3* may be considered good examples of standard all-hydrogenated shortening, and *2* may be considered typical of biscuit and cracker shortenings.

The above applies to hydrogenation wherein untreated, liquid oils are used as the starting material and hydrogenation is depended upon to give a product of proper consistency, without the necessity for further blending. Actually, in household shortening and in standard bakers' shortening many processors prefer to attain high-temperature body by blending in about 5% of stearine, either before or after hydrogenation. If this is done, hydrogenation may be conducted at a higher temperature and somewhat more selectively, since there will be little necessity for building up saturated acids during the process. At a higher temperature, hydrogenation will, of course, be considerably more rapid. Sometimes a blend of more than two stocks is made, with each being hydrogenated to a different degree, particularly if one of the softer stocks is to be made from soybean oil or other oil with a tendency toward flavor reversion. It may be mentioned that shortenings prepared by blending hard and soft stocks are never quite as low in iodine value as shortenings of equivalent body prepared by straight hydrogenation. For further information on the hydrogenation and blending of shortening stocks, see Chapter VIII.

Although all-hydrogenated and blended shortenings formerly comprised two entirely distinct types, hydrogenation has lately been extended to so many different products that from the manufacturing standpoint the distinction is no longer clear cut. Many shortenings marketed in the blended shortening price class are actually prepared by a combination of blending and hydrogenation. In making blended shortenings containing both cottonseed oil and soybean oil, for example, it is quite common practice to stabilize the soybean oil against flavor reversion by hydrogenating it to a maximum degree, while the more stable cottonseed oil may be hydrogenated relatively little. Shortenings containing tallow, as well as other blended shortenings, are often slightly hydrogenated after blending, to the extent of 1 to 10 units decrease in iodine value.

The hydrogenation of blended shortenings is naturally much less critical than that of shortenings of the all-hydrogenated type. It is usually carried out at a relatively high temperature, with catalyst which has previously been used in the hydrogenation of other products.

5. HYDROGENATION OF MARGARINE OILS

The hydrogenation of margarine oils, like that of all-hydrogenated shortenings, is a highly critical process, although the characteristics desired in the finished products are somewhat different. In the case of shortenings, it is desirable for the products to be as soft and plastic at the lower temperatures as is feasible, and at the same time have some body at a temperature in the neighborhood of 98°F. Margarine oils must be firm at lower temperatures, to simulate the consistency of butter, and in order that the margarine may be formed and packaged in the customary prints, but at the same time they must be plastic at atmospheric temperatures

TABLE 123

MARGARINE OIL MADE BY HYDROGENATION OF COTTONSEED OIL:
OPERATING AND ANALYTICAL DATA

Hydrogenation conditions:	
Temperature, °F	275
Pressure, lbs. per sq. in. gage	5
Catalyst, % nickel	0.08
Hydrogenation time, min	230
Iodine value	67.0
Composition of fatty acids:	
Saturated, %	26.5
Iso-oleic, %	20.8
Oleic, %	48.2
Linoleic, %	4.5
Micropenetrations, mm./10, at:	
45°F	15
70°F	65
80°F	140
90°F	295
98°F	Melted
Congeal point, °C	26.2

and must melt completely at the temperature of the human body, in order to not be "pasty" in the mouth.

The desired characteristics in margarine oil prepared from cottonseed or similar oils are obtained by choosing hydrogenation conditions which will produce much iso-oleic acid, but little saturated acids. Operating and analytical data covering the preparation of a commercial margarine oil from cottonseed oil are given in Table 123. It will be noted that the hydrogenation conditions listed in this table are similar to those of 2, Table 122 (biscuit- and cracker-type all-hydrogenated shortening), except that the reaction has been made even more selective, by reducing the

pressure from 50 to 5 pounds. This increase in selectivity is evidenced in a greatly increased formation of iso-oleic acid.

A product very similar to that of Table 123 can be made somewhat more conveniently, *i.e.*, with a shorter hydrogenation time, by raising the temperature to 300–325°F. and at the same time increasing the pressure to 30–40 pounds to compensate (in terms of selectivity) for the higher temperature. A considerable part of the margarine oil now manufactured is made under even more selective conditions, *i.e.*, at a temperature of 350°F. or above and about 5 pounds pressure, with a hydrogenation time of about one hour. In the hydrogenation of margarine oil with maximum selectivity, to produce a low-melting product, it is very important to use a highly selective catalyst, and to limit re-use of the catalyst. The most selectivity, to produce a low-melting product, it is very important to use content of 25% or more, an iodine value of about 70, and at a congeal point of 27.0–27.5°C., a Wiley melting point not in excess of 95°F. The less selectively hydrogenated oil referred to above will have a Wiley melting point of 96–98°F. in the same congeal point range.

Some margarine manufacturers prepare a stock somewhat harder than the product described in Table 123 and blend this with 10–20% of unhydrogenated, liquid oil. However, even with this method of manufacture, hydrogenation must be carried out quite selectively.

6. Hydrogenation of Hard Butter Substitutes

In the manufacture from liquid oils of hard butter substitutes suitable for confectionery coating, etc., the combination of relative hardness and nongreasiness at *ca.* 70°F. or below with substantially complete melting at body temperature is achieved by producing a large proportion of iso-oleic acids— in other words, such fats are essentially similar to very selectively hydrogenated margarine oils except that hydrogenation is carried somewhat farther. Peanut oil is considered a particularly suitable oil for making this type of product.

Ziels and Schmidt[38a] have patented a mthod of hydrogenating oils to produce a hard butter substitute which involves the use of a special catalyst which has been deliberately sulfur-poisoned. In one experiment cited, a fat quite similar in its physical characteristics to cocoa butter was prepared from peanut oil by hydrogenating with 0.5% nickel at 338°F. and 20 pounds pressure to an iodine value of 68.9. The melting point was 38.3°C. and the content of solids at 97°F. was but 3.2%, whereas the fat was quite hard up to about 80–85°F. and the solids content at 68°F. was 62.8% (as compared to about 64% for cocoa butter). The iso-oleic acid content of the product was 53.5%.

7. Hydrogenation of Inedible Fats and Fatty Acids

Fatty acids and inedible fats high in free fatty acids, when hydro-generated, are usually saturated as nearly as possible, although there is some partial hydrogenation of soft greases and marine oils for soapmaking. The hydrogenation of fatty acids is quite similar to the hydrogenation of vegetable oils to produce hard oils, except that temperatures above about 350°F. and sometimes above 300°F. are avoided, and high pressures are depended upon to accelerate the reaction. The convertors, which must be built of Type 316 stainless steel or other alloy resistant to corrosion, are usually designed for a working pressure of 200–300 pounds. Hydrogenation is relatively difficult; 0.2–0.5% of nickel is required, and the catalyst is largely inactivated with one usage.

8. Removal of Nickel from Hydrogenated Oils

Hydrogenated oils, and particularly those prepared with a wet-reduced catalyst, contain traces of nickel in the form of nickel soaps or colloidal metal which should be removed from edible products. Removal is accomplished usually by a so-called "post bleaching" step, in which the filtered oil from the converter, at a temperature of ca. 180°F., is treated with 0.1–0.2% of bleaching earth, preferably of the activated type, and filtered. A very small amount of phosphoric acid or other metal scavenger is sometimes added in the bleaching step. For the adsorption and removal of colloidal nickel, Borkowski and Schille[80a] recommend the use of activated carbon, which is added to the oil along with the catalyst, prior to hydrogenation. Carbon equal to 10 to 20 times the amount of nickel in the catalyst is said to yield a metal-free filtered oil and also to improve the color of the oil.

Oils intended for edible use are occassionally alkali-refined for nickel removal after hydrogenation, but this appears to be generally an unnecessary step.

H. Special Hydrogenation Processes

The foregoing has dealt only with the hydrogenation of ethylenic linkages in fatty acid chains to produce more highly saturated acids, esters, or glycerides, with hydrogen for the reaction being supplied in the molecular, gaseous form. In addition to this common hydrogenation process, there are a number of other catalytic hydrogenation reactions applicable to fats or their derivatives, some of which are of considerable technical importance.

1. HYDROGENATION TO PRODUCE FATTY ALCOHOLS

Alcohols of the higher fatty acids, such as lauryl alcohol, myristyl alcohol, palmityl alcohol, etc., are in considerable demand as intermediates for the manufacture of detergents and wetting agents of the sodium alkyl sulfate type (see p. 393, Ch. XI). These are prepared on a large scale by the catalytic hydrogenation of the corresponding acids, esters or glycerides, according to one of the following reactions: In the case of the acids:

$$RCOOH + 2 H_2 = RCH_2OH + H_2O$$
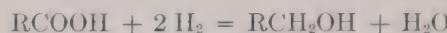
In the case of the esters of glycerides,

$$RCOOR' + 2 H_2 = RCH_2OH + R'OH$$

Priority with respect to the development of catalytic hydrogenation for the production of fatty alcohols is not clear. Apparently processes were developed at about the same time by Normann,[81] Schmidt,[82] and Schrauth, Schenk, and Stickdorn[83] in Germany, and Adkins and Folkers[84] and Lazier[85-87] in the United States. The basic United States patents on the process were granted to Lazier, and cover the hydrogenation of the fatty acids,[85] their esters with methyl, ethyl, or other monohydric alcohols,[86] and their glycerides.[87] An important feature of the Lazier patents is the use of catalysts of the copper chromite type first disclosed by Adkins and Connor[88] and patented by Lazier.[89] Ordinary nickel catalysts are said to be effective in the reduction of carboxyl groups at the high temperatures and pressures employed in the process, but the resulting products consist largely of hydrocarbons rather than alcohols. The fatty acid salts of a number of metals, including copper, zinc, lead, manganese, cobalt, and mercury, are claimed as catalysts in the patent issued to Schrauth and Böttler.[90]

Although fatty acids, esters, or glycerides may be used as the starting material for the production of fatty alcohols, the glycerides are perhaps generally preferred, because of the convenience in their use. The principal disadvantage in the use of glycerides is the circumstance that the glycerol produced as a by-product of the process is not stable under the conditions of the reaction, and hence cannot be recovered. If esters of monohydric alcohols are hydrogenated, the alcohols may be largely recovered. The

[81] W. Normann, Z. angew. Chem., 44, 714–717 (1931).
[82] O. Schmidt, Ber., B64, 2051–2053 (1931).
[83] W. Schrauth, O. Schenk, and K. Stickdorn, Ber., B64, 1314–1318 (1931).
[84] H. Adkins and K. Folkers, J. Am. Chem. Soc., 53, 1095–1097 (1931).
[85] W. A. Lazier (to E. I. du Pont de Nemours and Co.), U. S. Pat. 1,839,974 (1932).
[86] W. A. Lazier (to E. I. du Pont de Nemours and Co.), U. S. Pat. 2,079,414 (1937).
[87] W. A. Lazier (to E. I. du Pont de Nemours and Co.), U. S. Pat. 2,109,844 (1938).
[88] H. Adkins and R. Connor, J. Am. Chem. Soc., 53, 1091–1095 (1931).
[89] W. A. Lazier (to E. I. du Pont de Nemours and Co.), U. S. Pats. 1,964,000–01 (1934).
[90] W. Schrauth and T. Böttler (to "Unichem" Chemikalien Handels A.-G.), U. S. Pat. 2,023,383 (1935).

problem of alcohol recovery is avoided if fatty acids are employed as a starting material, but free acids are inclined to be corrosive to the hydrogenation equipment, and to enter into side reactions.

It has been observed by Guyer, Bieler, and Jadberg[91] that fatty acids of low molecular weight are much more difficult to hydrogenate to alcohols than are the higher acids. Thus, for example, in a series of comparable laboratory experiments covering the range of saturated acids from C_4 to C_{12}, lauric acid produced a 94% yield of alcohol with almost no ester or unchanged acid, whereas butyric acid produced but 10.9% alcohol, with 53.1% ester.

The hydrogenation is carried out by the batch method, at a temperature between 280° and 360°C. (536° and 680°F.), and at a pressure in the neighborhood of 3000 pounds per square inch. The catalyst, consisting of copper chromite, or copper chromite promoted with cadmium, cerium, etc., is used in the powder form, and agitation of the catalyst and reacting material is accomplished by circulation of the hydrogen.

Relatively high yields of alcohols are obtained; thus, for example, in the laboratory Adkins and Folkers[84] obtained yields of alcohols from the esters as high as 97.5–98.5%.

Ordinarily the reaction is not selective with respect to the reduction of carboxyl groups, i.e., unsaturated acids are hydrogenated to the corresponding saturated acids at the same time that hydrogenation of the carboxyl groups is accomplished. Under certain conditions, however, it may be reasonably selective. For example, in the laboratory Sauer and Adkins,[92] using a zinc chromite catalyst and a very high ratio of catalyst to fatty material, were able to obtain a 68% yield of unsaturated alcohols from oleic acid esters.

The use of alloy steel reactors is necessary in the hydrogenation of fatty materials to alcohols, to avoid corrosion of the equipment and metallic contamination of the product.

A somewhat different method of operation is employed in the so-called lead soap process, which is covered by a series of patents issued to Richardson and Taylor.[93] In this process the fatty acids are reacted with litharge to form lead soaps, and the latter are then treated with gaseous hydrogen, without the use of an additional catalyst, at a pressure in the neighborhood of 4000 pounds per square inch, and at a temperature in excess of 300°C. (e.g., 340°C.). Reaction occurs to produce alcohols in both the free and esterified forms, according to the following equations:

$$(RCOO)_2Pb + 5 H_2 \longrightarrow 2 RCH_2OH + 2 H_2O + Pb \quad \text{and}$$

$$(RCOO)_2Pb + 3 H_2 \longrightarrow RCOOCH_2R + 2 H_2O + Pb$$
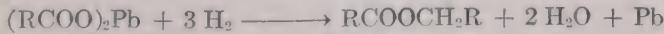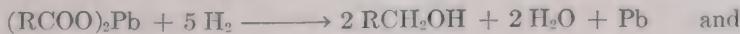
[91] A. Guyer, A. Bieler, and K. Jadberg, *Helv. Chim. Acta*, *30*, 39–43 (1947).
[92] J. Sauer and H. Adkins, *J. Am. Chem. Soc.*, *58*, 1–3 (1937).
[93] A. S. Richardson and J. E. Taylor (to Procter & Gamble Co.), U. S. Pats. 2,340,343–44 and 2,340,687–91 (1944); 2,375,495 (1945).

The lead is recovered in molten, metallic form. In a typical example given in one of the patents the reaction mixture from the treatment of lead oleate consisted of less than 1% oleic acid, about 21% oleyl oleate, and about 77% free oleyl alcohol. The product had an iodine value of 81, indicating that about 85% of the double bonds of the oleic acid had escaped saturation.

The lead soap process appears particularly desirable for the preparation of unsaturated fatty alcohols. Alternatively to lead, various other metals, notably cadmium, may be employed for forming the lead soaps, although less satisfactorily. The process is adaptable to continuous operation.

2. Fatty Alcohols by Sodium Reduction

The classical Bouveault-Blanc[94] method for producing fatty alcohols from the corresponding fatty esters by sodium reduction may be considered a variation of the hydrogenation process wherein hydrogen for reduction of the carbonyl group is derived from an alcohol through the action of sodium. The product of reduction consists of a mixture of sodium alkoxides which is hydrolyzed to obtain the free fatty alcohol, the glycerol or other alcohol with which the fatty acids were originally esterified, and the regenerated reducing alcohol.

The reaction is complex,[95] but the over-all result may be represented by the following typical equations, applying to interaction between triglycerides and ethyl alcohol:

$$C_3H_5(OOC.R)_3 + 12\ Na + 6\ C_2H_5OH \longrightarrow$$
$$3\ R.CH_2ONa + C_3H_5(ONa)_3 + 6\ C_2H_5ONa$$

and:

$$R.CH_2ONa + H_2O \longrightarrow R.CH_2OH + NaOH$$
$$C_3H_5(ONa)_3 + 3\ H_2O \longrightarrow C_3H_5(OH)_3 + 3\ NaOH$$
$$C_2H_5ONa + H_2O \longrightarrow C_2H_5OH + NaOH$$
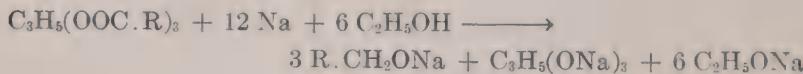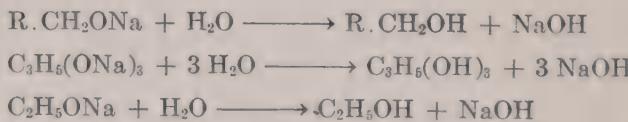
In commercial practice, one of the higher alcohols, e.g., methyl cyclohexanol or methyl amyl alcohol, is used as the reducing alcohol rather than ethyl alcohol. These may be safely used at a higher temperature than ethyl alcohol; they are less inclined to enter into side reactions, and in addition are easier to recover in an anhydrous form for re-use. A detailed description and discussion of an improved method employing theoretical quantities of reactants and an inert solvent (toluene, xylene) to increase the fluidity of the reaction mass, has been published by Hansley.[95] It is carried out at atmospheric pressure and at a temperature of about 140°C.

[94] L. Bouveault and G. Blanc, *Compt. rend.*, *136*, 1676–1678 (1903).
[95] V. L. Hansley, *Ind. Eng. Chem.*, *39*, 55–62 (1947).

Sodium reduction has been and is still used on a commercial scale for the production of fatty alcohols. It has the advantage over catalytic hydrogenation of effecting no change in the unsaturation of the fatty acid chain, and hence is particularly desirable for the manufacture of products containing a high proportion of unsaturated alcohols. The design and operation of a modern commercial plant operating on hydrogenated coconut oil have been described in a recent publication by Kastens and Peddicord.[95a]

3. Conjugated Hydrogenation

Conjugated hydrogenation refers to that variation of the hydrogenation process wherein the hydrogen is not supplied in a gaseous form, but is contributed by an alcohol, the alcohol being converted to an aldehyde in the process. The following reaction of a fat with propyl alcohol is typical:

$$CH_3CH_2CH_2OH + CH_3(CH_2)_xCH:CH(CH_2)_yR =$$
$$CH_3CH_2CHO + CH_3(CH_2)_xCH_2.CH_2(CH_2)_yR$$
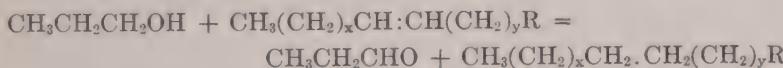
This process, so far as is known, has not attained technical importance, but it has been the subject of a considerable amount of investigation by Russian workers.[96,97]

Although in conjugated hydrogenation, as in ordinary hydrogenation, the composition of the hydrogenated fat is presumably influenced by the conditions of hydrogenation, the published analyses of hydrogenated oils would indicate that the method is inclined to be relatively selective, and to produce large proportions of iso-oleic acids. The following compositions were reported by Rush, Dvinianinkova, and Liubarskii[97] for sunflower oil hydrogenated at 260°C. with propyl alcohol and a nickel catalyst:

Saturated acids	12.5–14.8%
Oleic acid	50.8–56.3%
Iso-oleic acid	22.0–33.1%
Linoleic acid	3.6–10.3%

4. Hydrogenation of Nitriles to Produce Fatty Amines

A hydrogenation process of some technical importance is the hydrogenation of nitriles derived from fatty acids, to form amines. The process is carried out with a nickel or cobalt catalyst at temperatures and pressures which have not been made generally known.

Ordinarily both primary and secondary amines are produced, according to the following equations:

[95a] M. L. Kastens and H. Peddicord, *Ind. Eng. Chem.*, *41*, 438–446 (1949).
[96] E. I. Liubarskii, *J. Applied Chem. U.S.S.R.*, *5*, 1025–1045 (1932).
[97] V. A. Rush, I. L. Dvinianinkova, and E. I. Liubarskii, *J. Applied Chem. U.S.S.R.*, *10*, 702–708 (1937).

$$RCN \quad + \quad 2\,H_2 \quad = \quad RCH_2NH_2 \qquad\qquad (1)$$

Nitrile   Hydrogen   Primary amine

$$RCH_2NH_2 \quad + \quad RCN \quad + \quad 2\,H_2 \quad = \quad \begin{matrix} RCH_2 \\ \diagdown \\ NH \\ \diagup \\ RCH_2 \end{matrix} \quad + \quad NH_3 \qquad (2)$$

Primary amine   Nitrile   Hydrogen   Secondary amine   Ammonia
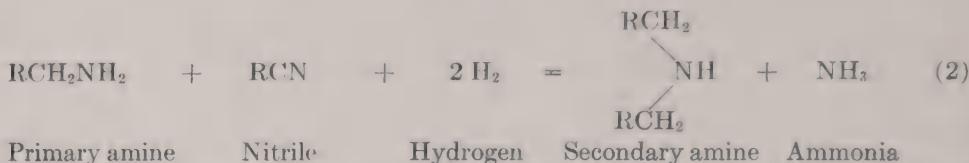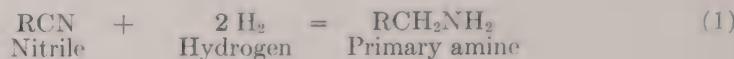
A maximum production of primary amines is generally desired, the secondary amines being merely an undesirable by-product. Production of secondary amines may be inhibited by the addition of gaseous ammonia to the hydrogenator at the beginning of the reaction, and the maintenance of a substantial pressure of ammonia relative to that of hydrogen as hydrogenation progresses.[98] It is claimed by Young and Christensen[99] that further improvement in the yield of primary amines, e.g., from about 50% to 70–80%, is obtained by the addition of water and caustic soda or other alkaline substance to the nitriles before the latter are hydrogenated. On the other hand, an increased yield of secondary amines can be obtained by using means to remove ammonia continuously from the reaction zone as the reaction proceeds.[100]

According to Kenyon, Stingley, and Young,[101] in commercial practice primary amines are obtained in yields of about 85% by hydrogenating with Raney nickel catalyst at 150°C. (302°F.) under 200 pounds pressure. For a maximum yield of secondary amines, higher temperatures and a different catalyst are employed. The use of a temperature of 285°F. and a pressure of 250 pounds is mentioned by Potts and McBride.[102]

[98] A. W. Ralston, *Oil & Soap, 17,* 89–91 (1940).
[99] H. P. Young and C. W. Christensen (to Armour & Co.), U. S. Pat. 2,287,219 (1942).
[100] H. P. Young (to Armour & Co.), U. S. Pat. 2,355,314 (1944).
[101] R. L. Kenyon, D. V. Stingley, and H. P. Young, *Ind. Eng. Chem., 42,* 202–213 (1950).
[102] R. H. Potts and G. W. McBride, *Chem. Eng., 57,* No. 2, 124–127 (1950).

DEODORIZATION

A. Introduction

1. HISTORICAL

Odorless and tasteless fats and oils first came into large demand as ingredients for margarine manufacture. Carefully rendered beef and hog fats are relatively neutral in flavor, and such flavor as these fats do possess is sufficiently animal-like in character as to be not too obtrusive in a butter substitute. The natural flavors of the vegetable fats, however, are relatively strong, and in addition are utterly foreign to that of butter.

In the latter part of the 19th century the demand for margarine fats in Europe grew to such proportions as to exceed the available supply of neutral animal fats. It was natural, under such circumstances, that a means should have been sought for rendering vegetable fats sufficiently neutral to permit their incorporation into margarine.

During the same period in which the new margarine industry was developing in northern and central Europe, there was a similarly rapid expansion in cotton production in the United States. The growing of cotton on a large scale resulted in the production of large quantities of cottonseed oil. In comparison with other vegetable oils, cottonseed oil is distinguished by an unusually high content of strongly flavored nonoil substances. Even after alkali refining it is still so unpleasantly flavored as to be virtually inedible without deodorization. Consequently, in order to make the American production of cottonseed oil available for edible purposes it was necessary from the beginning for the oil to be deodorized. The first use of steam deodorization in the United States is attributed to Henry Eckstein. The process was improved by David Wesson, who introduced the European practice of using vacuum-producing equipment in conjunction with steaming, and finally brought the process to its modern state of perfection by the combination of high vacua with high temperatures.[1]

Margarine did not immediately become popular in the United States. In fact, it is still relatively lacking in popularity throughout the Western Hemisphere. Deodorized cottonseed oil was soon used on a huge scale,

[1] For a more detailed account of the history of deodorization, see A. P. Lee and W. G. King, *Oil & Soap*, *14*, 263–269 (1937).

however, as an ingredient for lard substitutes or "shortenings," and to a lesser extent as a salad or cooking oil. Large quantities of soybean oil and other vegetable oils are now consumed in these products. Animal fats such as oleostearine, tallow, and lard have long been used in quantity in the manufacture of deodorized shortenings of the compound or blended type, with vegetable oils, and recently shortenings composed entirely of lard or lard and beef fat have begun to achieve some popularity on the American market. Hydrogenated and deodorized whale oil has long been one of the principal European margarine fats.

The present world-wide production of steam-deodorized fats and oils is probably not less than six billion pounds annually.

2. NATURE OF DEODORIZATION PROCESS

Steam deodorization is feasible because of the great differences in volatility between the triglycerides and the substances which give oils and fats their natural flavors and odors. It is essentially a process of steam distillation, wherein relatively volatile odoriferous and flavored substances are stripped from the relatively nonvolatile oil. The operation is carried out at a high temperature to increase the volatility of the odoriferous components. The application of reduced pressure during the operation protects the hot oil from atmospheric oxidation, prevents undue hydrolysis of the oil by the steam, and greatly reduces the quantity of steam required.

Few of the compounds responsible for tastes and odors in oils have been individually identified. Certain ketones, notably methyl nonyl ketone, have been identified in coconut oil, palm kernel oil, and cocoa butter.[2] Jasperson and Jones[3] have isolated terpenoid hydrocarbons from the deodorizer distillates of cottonseed, peanut, and sunflowerseed oils. Flavor and odor removal is observed generally to parallel free fatty acid removal. Thus, for example, if an oil has an initial free fatty acid content of 0.10%, the disappearance of noticeable flavor and odor will usually correspond to a reduction of the free fatty acid content to 0.02–0.04%. It is probable, therefore, that the vapor pressures and molecular weights of the odoriferous substances are of the same order of magnitude as those of the common fatty acids of 12 to 18 carbon atoms. In the operation of deodorizers in the plant it is often observed that the acidity of oils is reduced without adequate flavor removal.[4] However, in most such cases it seems probable that the operation is complicated by factors such as oxidation of the oil through inadequate deaeration or air leakage, excessive

[2] A. Haller and A. Lassieur, *Compt. rend.*, *150*, 1013–1019 (1910); *151*, 697–699 (1911). A. H. Salway, *J. Chem. Soc.*, *111*, 407–410 (1917).
[3] H. Jasperson and R. Jones, *J. Soc. Chem. Ind.*, *66*, 13–17 (1947).
[4] R. W. Bates, *J. Am. Oil Chem. Soc.*, *26*, 601–606 (1949).

condensation and refluxing of volatile materials, or short-circuiting of insufficiently deodorized oil through the deodorizing apparatus.
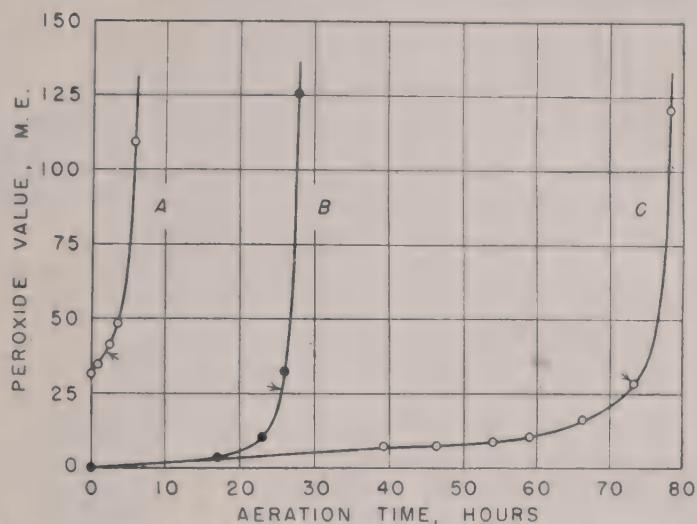
Fig. 127. Stability test curves (aeration at 110°C.) of (C) hydrogenated peanut oil, (A) the hydrogenated oil after oxidation to near-rancidity, and (B) the oxidized oil after steam deodorization.[5] (Arrows indicate points of organoleptic rancidity.)
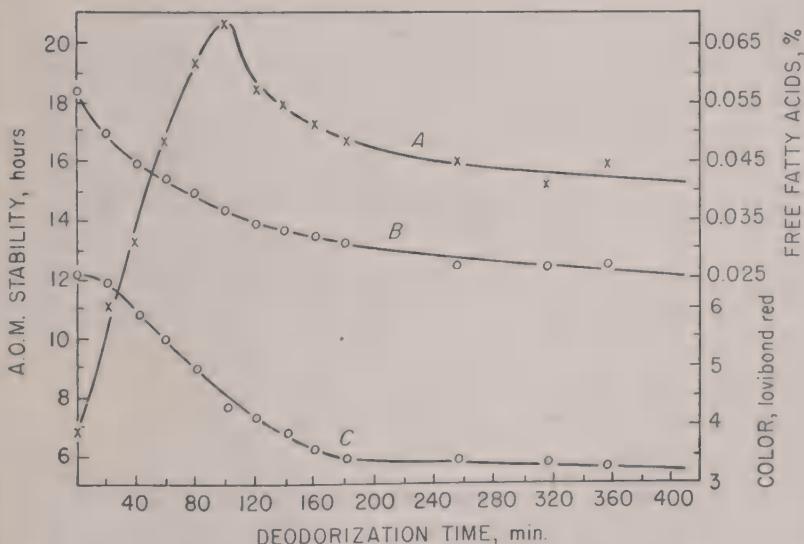
Fig. 128. Effect of laboratory deodorization at 419°F. and 8 mm. pressure upon: (A) the stability, (B) the acidity, and (C) the color of unhydrogenated corn oil.[6]

The concentration of odoriferous substances in an oil is generally quite low. In the case of common oils such as cottonseed oil, peanut oil, soybean

oil, tallow, and lard, it does not appear to be greater than about 0.10%. Hydrogenation of an oil imparts a decided flavor and odor. This odor appears to be characteristic of the hydrogenation reaction, as it is similar for different varieties of oil, and is developed even in oils which have been thoroughly deodorized previous to hydrogenation.

If deodorization is properly carried out, the removal of the odoriferous constituents from the oil is substantially complete. Well-deodorized oils of different kinds when fresh are virtually indistinguishable from one another by odor or taste, and merely give a sensation of oiliness in the mouth.

Deodorization also destroys any peroxides in the oil and removes any aldehydes or other volatile products which may have resulted from atmospheric oxidation. However, strongly rancid oils cannot be completely reclaimed by deodorization, as such oils will have lost most of their natural antioxidants through oxidation, and hence will become rancid a second time with relative ease. Typical stability tests[5] on oil, before and after partial oxidation, and before and after deodorization of the partially oxidized products, are shown in Figure 127.

The stability of vegetable oils of good quality is usually improved considerably by deodorization. Presumably, this is a result of the destruction of peroxides or other pro-oxidants, although the heat activation of antioxidants also seems a possibility, as animal fats do not generally respond similarly. However, animal fats are much more susceptible to incidental oxidation in the course of any processing treatment, because of their lack of natural antioxidants; hence it is difficult to make strict comparisons. In experiments with unhydrogenated corn oil, Baldwin[6] observed that when the oil was deodorized at 419°F. its stability increased to a maximum within 80–90 minutes, and thereafter declined slightly. His laboratory results are shown in Figure 128; essentially similar results were obtained in a large-scale experiment using a commercial batch deodorizer. Apparently the initial increase was a heat effect independent of steam stripping, as a similar improvement in stability was obtained by simply heating the oil under vacuum.

In agreement with general experience in laboratory and plant practice,[7] Riemenschneider and co-workers[8] found that laboratory deodorization did not improve the keeping quality of prime steam lard; however, mild deodorization (356°F. for one hour) increased the A.O.M. stability of a sample of kettle-rendered lard from 7 hours to 12 hours.

[5] A. E. Bailey and R. O. Feuge, *Oil & Soap*, 21, 286–288 (1944).
[6] A. R. Baldwin, *J. Am. Oil Chem. Soc.*, 25, 33–35 (1948).
[7] See, for example, H. E. Robinson and H. C. Black, *Ind. Eng. Chem.*, 37, 217–219 (1945).
[8] R. W. Riemenschneider, S. F. Herb, E. M. Hammaker, and F. E. Luddy, *Oil & Soap*, 21, 307–309 (1944).

Because of the instability of carotenoid pigments to heat, deodorization markedly reduces the color of most vegetable oils, particularly if the color has not been greatly reduced by bleaching and if it is contributed largely by pigments of this type, as is the case, for example, with soybean and corn oils (see Fig. 128). Even bleached and hydrogenated shortening and margarine oil stocks made largely or entirely from cottonseed oil commonly lose 10–30% of their red color upon deodorization. The bleaching effect depends upon both the time and temperature of deodorization. Whereas 2–4 hours may be required to achieve maximum decolorization at 400–425°F. (see Fig. 128), no more than 45–60 minutes is usually required at 440–460°F.

Various methods other than steam deodorization have been proposed for rendering edible oils odorless and tasteless, but none, so far as the author is aware, have ever found commercial application. Treatment of oils with activated carbon or other adsorbents is of very limited value for flavor or odor removal. In steam deodorization the stripping steam serves merely as a carrier for the substances to be distilled from the oil, and does not necessarily exert any chemical action on the oil. Any other inert gas, such as hydrogen or nitrogen, would serve equally well if it were as cheap as steam and if it could be condensed and thus easily removed from the deodorizer system.

The free fatty acids of an oil are usually more or less completely removed by deodorization. When the primary object is the removal of free acids, rather than flavor and odor, the process is termed "steam refining." The level to which the free fatty acid content of an oil can be reduced by deodorization is about the same as that produced by alkali refining, i.e., about 0.015–0.03%. Even under a high vacuum the stripping steam has a slight tendency to split the oil, with the formation of free acids. The rate at which splitting occurs bears no relation to free acid concentration, at low levels of the latter. On the other hand, the rate at which the free acids distill is directly proportional to their concentration in the oil. Consequently, as their concentration decreases, a point is eventually reached where the rate at which they are removed is equalled by the rate at which they are formed.

B. Theoretical Considerations

1. Theory of Steam Stripping[9]

If it is assumed that the system comprising an undeodorized oil and its associated volatile impurities conforms to Raoult's law, the vapor

[9] See also the following: W. Brash, J. Soc. Chem. Ind., 45, 73–75, 331–333T (1926); A. E. Bailey, Ind. Eng. Chem., 33, 404–408 (1941); H. J. Garber and F. Lerman, Trans. Am. Inst. Chem. Engrs., 39, 113–131 (1943); R. W. Bates, J. Am. Oil Chem. Soc., 26, 601–606 (1949).

pressure of any volatile component will be equal to its vapor pressure in pure form at the temperature in question multiplied by its molar concentration in the oil. Mathematically:

$$p_v = P_v \left(\frac{V}{O + V} \right)$$

(1)

where p_v = equilibrium pressure of the volatile component in the oil, P_v = vapor pressure of the pure volatile component, V = mols of the volatile component, and O = mols of oil. However, V is extremely small in relation to O, so that $O + V$ closely approaches the value of O. Therefore, as a close approximation of equation (1) we may write:

$$p_v = P_v . V/O$$

(2)

According to Dalton's law, in the vapors issuing from the deodorizer at any instant the molar ratio of volatile substance to steam will be the same as the corresponding ratio of their partial vapor pressures. Mathematically:

$$\frac{dS}{dV} = \frac{p_s}{p'_v}$$

(3)

where V = mols of volatile component, as before, S = mols of steam, p_s = actual partial pressure of the steam, and p'_v = actual partial pressure of the volatile component. But p'_v is very small in comparison with p_s, so p_s closely approaches the total pressure. Consequently as a close approximation of equation (3) we have:

$$\frac{dS}{dV} = \frac{P}{p'_v}$$

(4)

where P = the total pressure, or $p'_v + p_s$.

At this point a new factor, E, the vaporization efficiency, may be introduced. By definition:

$$E = \frac{p'_v}{p_v}$$

(5)

Combining equations (2) and (5):

$$p'_v = EP_v V/O$$

(6)

Finally, from equations (4) and (6):

$$\frac{dS}{dV} = \frac{PO}{EP_v V}$$

(7)

Integrating equation (7):

$$S = \frac{PO}{EP_v} \left(\ln \frac{V_1}{V_2} \right) \tag{8}$$

where V_1 = initial concentration of volatile substance in the oil, and V_2 = final concentration of volatile substance in the oil.

The amount of steam required for deodorization (or the time required at a definite steaming rate) is thus seen to be: (a) directly proportional to the size of the oil batch; (b) directly proportional to the absolute pressure in the deodorizer; (c) inversely proportional to the vapor pressure of the pure volatile or odoriferous components at the temperature of operation; (d) inversely proportional to the vaporization efficiency; and (e) directly proportional to the logarithm of the ratio of initial to final concentration of volatile substances.

Practically speaking, the vaporization efficiency is a measure of the completeness with which the steam becomes saturated with volatile substances during its passage through the oil. From the two-film theory of gas absorption of Whitman[10] it follows that at any instant the rate of transfer of volatile substance from the oil into a steam bubble is equal to the difference between saturation pressure in the bubble and actual pressure, times the surface area of the bubble, times a constant characteristic of the oil and the steam. Mathematically:

$$dp_v'/dt = kA(p_v - p_v') \tag{9}$$

where t = time of contact between steam bubble and oil, A = surface area of the steam bubble, and k = gas diffusion constant.

Integrating equation (9):

$$Akt = \ln \left(\frac{p_v}{p_v - p_v'} \right) \tag{10}$$

$$= \ln \left(\frac{1}{1 - \dfrac{p_v}{p_v'}} \right)$$

$$= \ln \frac{1}{1 - E} \tag{11}$$

$$\text{or} \quad E = 1 - e^{-Akt} \tag{12}$$

The vaporization efficiency thus increases with an extension of the total surface area of the steam bubble and with the time of contact between steam bubbles and oil.

The above Equations (1) to (8) apply strictly only to ideal solutions of foreign materials in the oil. Virtually all real systems deviate to some

[10] W. G. Whitman, *Chem. & Met. Eng.*, *29*, 146–148 (1923).

degree from ideality, and for these the vaporization efficiency calculated from Equation (8) will be higher than the true value if there is negative deviation from ideality and lower if there is positive deviation. There are no analytical methods available for quantitatively evaluating the apparent vaporization efficiency with respect to the odoriferous components of the oil, but there are some data based upon the stripping of free fatty acids. In the batch deodorization (steam refining) of palm oil, rough estimates of the vaporization efficiency have ranged from 0.7 to 0.9.[11] In a special apparatus simulating conditions in a commercial deodorizer of semicontinuous design, a value of 0.99 was obtained with a hydrogenated lard product high in free fatty acids, and a value of 0.82 was obtained with cottonseed oil to which distilled C_{18} acids had been added.[12]

Altogether, it seems probable that an oil containing a moderate proportion of free fatty acids does not deviate greatly from ideality, and hence that the maximum apparent vaporization efficiency is not far from unity. That this is so and that reasonably high vaporization efficiencies are actually obtained in commercial practice appears to be indicated by the fact that there is no correlation between pressure and calculated vaporization efficiency in commercial deodorization within the pressure range of about 6–25 mm. Eight and one-half feet of oil in the average batch deodorizer exerts a hydraulic pressure equivalent to about 190 mm. of mercury. Each bubble of steam during its passage through the oil is therefore subjected to a constantly varying external pressure, with a corresponding variation in its volume and area. A high vacuum serves not only to make the average steam bubble comparatively large, thus making its surface area small in proportion to its volume, but also makes its average volume during its passage through the oil small in proportion to its final volume at the surface of the oil. Vaporization efficiency is based upon instantaneous conditions applying at the *surface* of the oil; therefore it should decrease as the vacuum increases. That it apparently does not would indicate that saturation of the steam bubble at high temperatures is so rapid as to be substantially complete at any pressure down to at least 6 mm.

Regardless of the reliability of the calculated vaporization efficiences as absolute values, they furnish an adequate measure of the *comparative* efficiency of stripping and of steam utilization under different conditions, and thus are valuable aids in the design of deodorizing equipment.[12]

Since the rate at which free fatty acids or other volatile components are being stripped from an oil under fixed conditions of temperature, pressure, and steam flow is proportional to their concentration in the oil (Equation 7), it follows that a plot of the logarithm of the concentration

[11] A. E. Bailey, *Ind. Eng. Chem.*, *33*, 404–408 (1941).
[12] A. E. Bailey, *J. Am. Oil Chem. Soc.*, *26*, 166–170 (1949).

against deodorizing time should yield a straight line. Actually, as will be seen from Figure 129, linear curves are obtained in fatty acid stripping down to a free fatty acid content of 0.10–0.20%. As the free fatty acid content cannot be reduced indefinitely, but at low pressures will eventually level off at a value of about 0.01–0.03%, and as the pressure within the deodorizer determines the point at which deviation from linearity begins, the departure from linearity in the lower ranges of acidity may be reasonably attributed to hydrolysis of the oil by the stripping steam, which builds up free acids at a rate which eventually approaches their rate of removal. It is conceivable that there may also be a negative departure
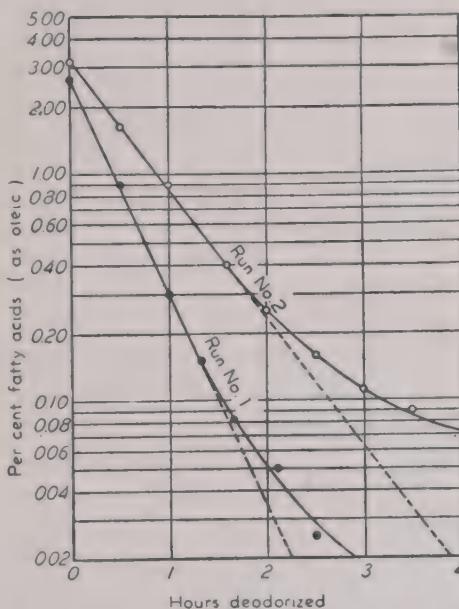
Fig. 129. Removal of free fatty acids from palm oil by steam deodorization.[11] Run No. 1—19,000 lbs. oil, 400 lbs. per hour steam, 460°F., 10 mm. pressure. Run No. 2—18,400 lbs. oil, 800 lbs. per hour steam, 460°F., 25 mm. pressure.

from ideality in the system, which becomes greater as the concentration of free acids is reduced. However, the possibility of any large negative deviation appears to be ruled out by the high calculated values for vaporization efficiency mentioned above.

If the stripping steam and the oil pass each other continuously in countercurrent flow, as in one of the commercial continuous deodorization systems, the mathematical analysis becomes more involved. Equations comparable to those given above for noncountercurrent operation have been published by Garber and Lerman[13] (see also Bates[4]).

[13] H. J. Garber and F. Lerman, *Trans. Am. Inst. Chem. Engrs.*, *39*, 113–131 (1943).

2. Oil Losses in Deodorizing

The amount of odoriferous compounds required to be removed in deodorizing an edible oil is small, probably seldom, if ever, exceeding 0.1% of the weight of the oil. However, in steam deodorization there is an unavoidable loss of other materials, which makes the total loss considerably greater. In any case the loss of material by distillation will depend upon the time, steaming rate, pressure, and temperature of deodorization, as well as the amount of free fatty acids and unsaponifiable material in the oil, and the composition of the glycerides. In most batch deodorizers the distillation of volatile materials is complicated by considerable condensation and refluxing from the upper portions of the apparatus, and frequently there is a significant loss of oil by mechanical entrainment in the stripping steam. Consequently, the losses in different plants and with different oils are quite variable. However, in modern plants where mechanical entrainment is minimized and vegetable oils containing less than 0.1% free fatty acids are deodorized at 5–10 mm. pressure and at 400–475°F. (204–246°C.) to yield completely bland products, the loss of material from the deodorizer is generally between about 0.3% and 0.8%.

(a) Losses by Distillation

The most easily distilled materials in fats and oils are free fatty acids, which have vapor pressures (in the case of C_{16} and C_{18} acids) of the order of 5–50 mm. at deodorizing temperatures. Ordinarily, the free fatty acids in an oil are removed by deodorization almost completely; hence it is assumed that the deodorizing loss must include any free acids that are present. In addition, there is a small loss due to the distillation of fatty acids that are derived from oil split by the stripping steam. As the rate at which free fatty acids are produced by hydrolysis usually matches the rate at which they are removed by distillation at a level of about 0.015–0.030%, it can be calculated from Equation (7) and the data given previously on apparent vaporization efficiencies, that in cottonseed oil each pound of stripping steam must set free and strip out about 0.008–0.016 pound of fatty acids at 6 mm. pressure and 410°F. (210°C.) and about 0.024–0.048 pound of fatty acids at 460°F. (238°C.) and 6 mm. pressure. With allowance for a certain amount of refluxing in a commercial batch deodorizer, these calculated losses are in reasonably good agreement with losses actually observed. In a series of experiments in which low-acid stocks were deodorized and estimates of the amounts and composition of distilled fatty material were made from analyses of barometric condenser water,[11] the observed losses in terms of pounds of free fatty acids per pound of stripping steam were as follows: at 410°F. and 10 mm., 0.005–0.012; at 460°F. and 10 mm., 0.008–0.011.

Actually, commercial deodorization is conducted under such conditions that losses in the form of fatty acids are not usually more than 20–30% of the total loss.

The sterols and other unsaponifiable materials in oils are for the most part much less volatile than the free fatty acids, but in refined oils they are present in greater amount, and they may constitute an appreciable proportion of the fatty material distilled from the oil. According to Neal,[14] severe deodorization at a very high temperature may reduce the unsaponifiable content of an oil such as soybean oil by as much as 60%, but the proportion is less in ordinary commercial practice.

The glycerides are very much less volatile than the other constituents
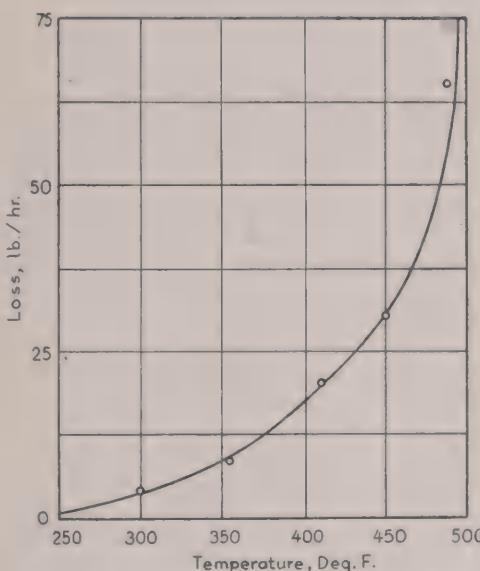
Fig. 130. Loss of neutral oil through distillation in batch deodoriza-tion.[11] Hydrogenated cottonseed oil, 20,000 lb. batch, steaming rate, 350 lbs. per hour, pressure 10 mm.

of a fat or oil, but since they constitute the bulk of the oil, they are dis tilled out in deodorization in appreciable amounts. The distillation losses of neutral oil, i.e., glycerides plus unsaponifiable matter, in the commer-cial batch deodorization of hydrogenated cottonseed oil have been meas-ured by the author and found to be approximately as follows, in terms of pounds of material carried by each pound of stripping steam: at 410°F. (210°C.) and 25 mm. pressure, 0.018; at 460°F. (238°C.) and 25 mm. pressure, 0.057; at 410°F. and 10 mm. pressure, 0.035; at 460°F. and 10 mm. pressure, 0.11. These experiments were carried out under

[14] R. H. Neal (to The Best Foods, Inc.), U. S. Pat. 2,351,832 (1944).

conditions that minimized, but probably by no means prevented, reflux within the deodorizer. Distillation losses may be greater without reflux and they are certainly less in installations where considerable refluxing occurs. Other typical distillation loss tests in batch deodorization are shown in Figure 130.[11]

The amount of neutral oil distilled in deodorization appears to vary considerably with different oils. Losses in deodorizing soybean oil or soybean oil products are consistently less than in deodorizing cottonseed oil products, for example. Coconut oil, which has a low average molecular weight, suffers still higher losses than cottonseed oil under comparable deodorization conditions. In view of the very low vapor pressures that have been reported for triglycerides (see page 93), it appears possible that diglycerides, either preformed or produced by hydrolysis during deodorization, may enter largely into deodorization losses by distillation.

(b) Loss by Entrainment

Mechanical entrainment of oil by the stripping steam is the source of an appreciable loss of oil in many deodorizer installations. The stripping steam rising through the upper portion of the conventional batch deodorizer probably does not have a sufficiently high velocity to carry oil droplets upward from the surface of the deodorizer in any appreciable amount. However, in expanding into the oil and from the oil surface the steam expends a considerable amount of kinetic energy, and this energy is sufficient to throw droplets of oil upward into the vapor outlet or other constricted vapor passages, where the vapor velocity will be great enough to carry them forward and out of the deodorizer.

The amount of entrainment occurring in any case is related to the density as well as the velocity of the steam. Souders and Brown[15] have given the following expression for the critical velocity of vapor required for carrying droplets of a given size:

$$v = KD^{1/2}\left(\frac{d_1 - d_2}{d_2}\right)^{1/2} \tag{13}$$

where v = linear velocity of the vapor (steam), D = diameter of droplet, d_1 = density of droplet, d_2 = density of vapor, and K = a constant. In this equation, the magnitude of d_2 is very small in relation to that of d_1. Consequently, as an approximation of equation (13) we may write:

$$v = KD^{1/2} d_1^{1/2} (1/d_2^{1/2}) \tag{14}$$

At a given temperature d_1 is constant, hence $d_1^{1/2}$ and K may be combined in a new constant K'. Equation (14) then becomes:

[15] M. Souders and G. G. Brown, Ind. Eng. Chem., 26, 98–103 (1934).

$$v = K'(D^{1/2}/d_2^{1/2}) \tag{15}$$

It will thus be seen that the steam velocity required to entrain oil droplets varies with the square root of the diameter of the droplet. The weight of the droplets, however, varies with the third power of the diameter. Therefore the weight of the largest droplets of oil that will be entrained varies with the sixth power of the steam velocity or flow. The weight of the largest droplets does not, of course, correspond to the actual weight of oil entrained per unit time, but it is obvious that entrainment must increase very rapidly with increase in the steam flow. The data shown
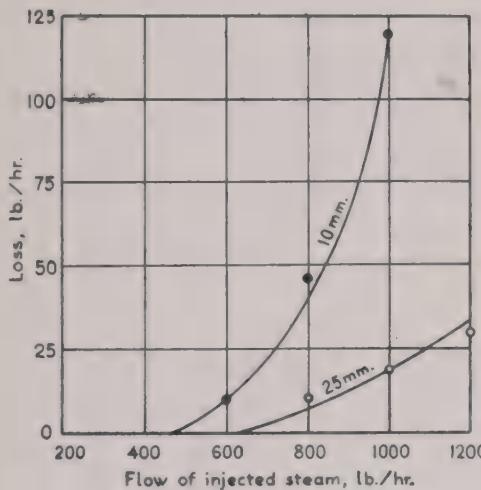
Fig. 131. Loss of oil through entrainment in batch deodorization.[11]

graphically in Figure 131, illustrate the rapidity with which entrainment losses increase when the rate of steaming is carried to high levels.

3. Influence of Different Operating Variables

(a) Influence of Temperature

The temperature at which deodorization is conducted has a very great effect upon the amount of steam required, and consequently the time consumed in the operation.

It was noted previously that the steam requirements are inversely proportional to the vapor pressure of the pure volatile components of the oil, at the operating temperature. According to the Clausius-Clapeyron equation relating the vapor pressure of a substance to its temperature, the *logarithm* of the vapor pressure of the volatile constituents is within a limited range approximately proportional to its absolute temperature. Thus if a given increment in temperature will double the volatility of the

odoriferous substances, a further like increment will quadruple their volatility, etc.

The rapid increase in vapor pressure which is caused by an increase in temperature is illustrated by the following values for the vapor pressure of palmitic acid at different temperatures[16]: at 350°F., 1.8 mm.; at 400°F., 7.4 mm.; at 450°F., 25 mm.; at 500°F., 72 mm. The slope of the vapor pressure–temperature curves for volatile substances other than fatty acids are unknown but it is unlikely that they are greatly different from those of palmitic and other fatty acids. Thus by increasing the temperature of deodorization from 350°F. (177°C.) to 400°F. (204°C.), the rate at which odoriferous substances are removed from the oil can be expected approximately to triple, and a further tripling in the rate can be expected by raising the temperature to 450°F. (232°C.). Stated in another way, for a given standard of flavor and odor in the finished product about three times as long will be required to deodorize at 350°F. as at 400°F., and nine times as long will be required as at 450°F.

In actual operation the variation in time required for deodorization will be found to be quite close to that predicted above.

(b) Influence of Vacuum

The amount of steam required for deodorization, as noted previously, is directly proportional to the absolute pressure. Hence for the most economical operation the vacuum should be as high as possible. A pressure of 0.25 inch (6 mm.) or better is easily obtainable with well-designed three-stage steam ejector equipment. If, through the use of poor vacuum equipment or poor operation of the equipment, a pressure no lower than 0.5 inch can be obtained, the steam requirements will be doubled; if a pressure no lower than 1.0 inch can be obtained, they will be quadrupled.

The vacuum also has an important effect on the time required to complete the deodorization. If, for example, steam is to be injected at a maximum rate of 350 pounds per hour at a pressure of 0.25 inch without excessive entrainment, it follows from equation (15) that the maximum permissible rate of steaming at a pressure of 1.0 inch is twice as great, or 700 pounds per hour. However, the weight of steam required for deodorization at 1.0 inch is four times that required at 0.25 inch; hence twice as long will be required to deodorize at the higher pressure.

The inhibiting effect of high vacuum on hydrolysis of the oil during deodorization is also somewhat important. As mentioned previously, hydrolysis is a factor in determining distillation losses, and even slight hydrolysis will make it difficult to obtain a low free fatty acid content in the finished deodorized oil. In some cases the deodorization operation may be depended upon to effect a certain degree of refining of the oil. For

[16] W. O. Pool and A. W. Ralston, *Ind. Eng. Chem.*, *34*, 1104–1105 (1942).

example, it may be desired to produce a finished oil with 0.01–0.03% of free fatty acids from an oil which initially contains 0.1–0.2% of acids. The marked influence of pressure on the attainment of low free fatty acid contents in the oil is evident from Figure 129. A high vacuum in deodorizing is advantageous in every respect. It leads to economy of operation, more rapid deodorization and a lower content of free fatty acids in the finished oil.

(c) Influence of Steaming Time and Rate

In ordinary batch deodorization, the efficiency of stripping steam utilization, i.e., the vaporization efficiency, appears to vary little with the steaming rate, at least within normal limits of the latter. However, in baffled apparatus of the continuous or semicontinuous types (pages 792–794), where the oil is stripped in shallow layers and splashing of the oil against baffles is depended upon to break up the oil and steam and create a large oil–steam interface, the vaporization efficiency increases with the steaming rate. In any case, the steaming rate must, of course, be held below that at which appreciable mechanical entrainment begins to occur.

The time required for efficient deodorization appears to be simply that in which sufficient steam can be passed through the oil to reduce the odoriferous components to a desired low level. Although it has often been suggested that polymerization or other heat alteration of these components occurs,[17] and that there is thus a minimum time as well as a minimum amount of stripping steam for good deodorization, there appears to be little positive evidence to support such a view, at least in the case of ordinary vegetable and animal fats. At any rate, the minimum does not exceed one hour, as at high temperatures highly efficient deodorization is achieved in modern apparatus within this time.[12]

With the pressure and steaming rate fixed, the time required for a given standard of deodorization appears to vary approximately in inverse proportion to the vapor pressure of volatile materials in the oil, as judged on the basis of the vapor pressures of the common fatty acids. Therefore, the time is halved with each increase in the temperature of about 30°F. or 17°C.

(d) Influence of Deodorizer Design

Theoretically, less hydrolysis of the oil should occur and it should be possible to reduce the fatty acids content of oil to a lower value when stripping is carried out in shallow layers than when the oil is in a deep layer and the average hydraulic pressure of the oil upon the injected steam bubbles is relatively high. Comparative results in which stripping is

[17] See, for example, C. E. Morris, J. Am. Oil Chem. Soc., 26, 607–610 (1949).

carried out in layers of oil varying from a few inches to several feet in depth do, in fact, reveal a slight trend toward lower acidities at the lesser oil depths. However, the factor of oil depth appears to be rather less important in this respect than does the absolute pressure above the oil. As mentioned previously, deodorization in efficient batch equipment at about 6 mm. pressure can be depended upon to reduce the free fatty acids content of most oils to about 0.015–0.030%, and there is no very significant difference in oils deodorized in continuous or semicontinuous equipment where the depth of oil is less.

If the deodorizer is so designed as to have extensive cool surfaces above the surface of the oil, upon which volatile materials may condense and then return to the oil, the efficiency of stripping with respect to all volatile constituents may be very seriously impaired.[18]

C. Design and Operation of Deodorization Equipment[18a]

1. GENERAL DESIGN FEATURES

(a) *Equipment for Production of Vacuum. Steam Consumption*

For the maintenance of vacuum on virtually all modern deodorizers use is made of multistage steam ejectors with barometric intercondensers. Surface condensers are unsatisfactory because of fouling of their surfaces by fatty material carried by the stripping steam, and mechanical vacuum pumps are both more expensive and more difficult to operate and maintain than steam ejectors.

Three-stage ejectors are more or less standard equipment. A good three-stage system, consisting of a large primary condensing ejector or booster, a secondary small condensing ejector, and a third noncondensing ejector for the discharge of noncondensable gases, will maintain an absolute pressure of 5–6 mm. For the production of lower pressures, *e.g.*, 1–2 mm., a fourth stage consisting of a second noncondensing booster back of the first is required. It is generally considered that the advantages of the lower pressure are not commensurate with the additional steam consumption of the added stage, although a number of four-stage units are in operation. On the other hand, operation of deodorizers at a pressure much above 6 mm. is likewise wasteful of steam, and is usually considered undesirable.

The amount of steam required for operation of the ejectors is always several times the amount of stripping steam, and all steam must be condensed; hence steam and cooling water requirements for deodorizing are

[18] See G. W. Phelps and H. C. Black (to Industrial Patents Corp.), U. S. Pat. 2,407,616 (1946).

[18a] See also J. W. Bodman, E. M. James, and S. J. Rini, Chapter XVII. in *Soybeans and Soybean Products*, K. S. Markley, ed., Interscience, New York. 1950.

heavy. The ratio of ejector steam to stripping steam varies somewhat according to the size of the ejectors, the steam pressure, the temperature of the condenser water, and the amount of water used, but in the case of modern three-stage ejector systems designed to operate with steam at 150 pounds pressure and cooling water at 85°F. (a common summer cooling tower temperature), and to maintain an absolute pressure of 6 mm., it is commonly about 3.75 to 1. Under these conditions, the consumption of cooling water is about 15 gallons per pound of total steam. In operation, steam ejectors are relatively inflexible, *i.e.*, their steam consumption cannot be reduced with reduction of the stripping steam load. It is undesirable, furthermore, to release the vacuum on deodorizers while they are empty; hence much steam is consumed in the maintenance of vacuum during heating, cooling, and pumping of the oil charge, and during "down" periods when steam stripping is not actually progressing.

In complete plants which process crude vegetable oils into finished shortening, salad and cooking oils, or margarine, the operation of batch deodorizers often accounts for as much as 50% of the total steam consumed in the plant. The newer continuous and semicontinuous deodorization systems have been developed with the object of reducing this large steam and water consumption quite as much as to effect improvement in the quality of the product.

(b) Heating and Cooling of the Oil

As temperatures of 400–475°F. (204–246°C.) are required for rapid and efficient deodorization, ordinary steam boilers producing steam for processing at about 150 pounds pressure (366°F.) cannot be used for heating oil for deodorization.

A number of different methods have been devised for heating the oil to a high temperature. Because of the low ratio of surface to volume in vessels of large capacity it is not practicable to heat large deodorizers by direct firing. A system has been considerably used, however, in which the batch of oil is heated by circulating it from the deodorizer through a system of tubes in an external furnace, the latter being heated by direct gas firing. Sufficiently high temperatures are attained by this method, but it has the serious disadvantage of subjecting portions of the oil to temperatures far above the actual temperatures required for deodorization. Even with the most rapid and efficient circulation of oil through the tubes, the film of oil on the walls of the latter will reach a temperature greatly in excess of the average temperature of the circulating oil. This effect is to some degree injurious to the product, and it also results in slow deposition of a coating of polymerized oil on the inside of the heating-tube walls, necessitating periodic cleaning of the latter. Other disadvantages are the

difficulty of maintaining circulation of the hot oil with the complete elimination of "dead spots" in the heating zone, and the likelihood of seriously injuring the batch of oil in the event of the accidental break-down of the circulating system.

An alternative heating system which has also been widely used in the past utilizes a special, heat-stable mineral oil as a heat-transfer medium.[19] The mineral oil is heated by direct gas firing, in a furnace similar to the one described above, and is circulated through heating pipes inside the deodorizer. In this system, as in the previous one, there are difficulties in maintaining rapid and turbulent flow throughout the heating zone. There is, moreover, a considerable tendency for even the most stable mineral oil to undergo decomposition in service. A large amount of surface is required for heat transfer between the heating oil and the fatty oil, as the trans-mission of heat from the former is much less efficient than that from a condensing vapor is in heating with steam.

Other methods which have been successfully used for attaining high temperatures for deodorizing include the use of special high-pressure steam boilers, and steam compressors. The use of superheated steam for heating oil to high temperatures is not practicable, as in this method only the rela-tively slight sensible heat of the steam is available for heating the oil, the latent heat of the steam of course not being available.

A much more satisfactory heating method than any of the preceding, and one which is now used in virtually all new deodorizer installations in the United States, is the Dowtherm system.[20,21] Dowtherm, the trade name of the eutectic mixture of diphenyl and diphenyl oxide, has a boil-ing point of 495.8°F. (257.7°C.) at atmospheric pressure and 560°F. (293°C.) at only 16.1 pounds gage pressure; hence by using its vapors for heating, adequate temperatures are achieved at low pressures. Dowtherm systems for heating deodorizers are simple—the vaporizer is connected to heating coils or heat exchangers to form a closed system, and usually condensate is returned to the vaporizer by gravity, as the necessity for elevating the barometric condensers on the ejector system usually insures a sufficient elevation of the heating surfaces to provide satisfactory return by this method. Pressures of 15–30 pounds gage are commonly main-tained on the vaporizer. Dowtherm heating is not essentially different from heating by steam, though the low heat of vaporization of Dowtherm requires special provision for handling large volumes of vapor and con-densate, and the system must be kept completely dry and free of air

[19] See J. P. Harris and A. B. McKechnie, *Oil & Fat Ind.*, *4*, 371–377 (1927); A. B. McKechnie, *Ind. Eng. Chem.*, *21*, 496–498 (1929).
[20] The Dow Chemical Co., *The Dowtherm Story*. Midland, Mich., 1948.
[21] The Foster Wheeler Corp., Bulletin ID-46-3 "Dowtherm Heating Systems," New York, 1946.

as the presence of either air or water vapor will interfere with the proper circulation of heating vapors.

The properties of Dowtherm vapor in the range of ordinary working pressures are given in Table 124.[20] Dowtherm is noncorrosive to ordinary metals of construction, and relatively nontoxic, and in properly designed systems its rate of thermal decomposition is almost negligible.

TABLE 124

PROPERTIES OF DOWTHERM A (DIPHENYL–DIPHENYL OXIDE) VAPORS[a]

| Temp., | | Pressure, lbs./in.² | | Heat content, B.t u./lb. | | | Spec. heat liquid | Density, lbs./ft.³ | |
°F.	°C.	Abs.	Gage	Liquid	Latent	Total		Liquid	Vapor
495.8	257.4	14.7	0	217.8	125.0	342.8	0.63	53.2	0 262
500	260.0	15.65	0.95	220.5	124.5	345.0	0.63	53.1	0.275
510	265.6	17.8	3.1	226.8	123.6	350.4	0.63	52.7	0.305
520	271.1	19.9	5.2	233.0	122.6	355.6	0.64	52.4	0.337
530	276.7	22.3	7.6	239.4	121.6	361.0	0.64	52.0	0.372
540	282.2	24.9	10.2	245.9	120.5	366.4	0.64	51.7	0.409
550	287.8	27.7	13.0	252.6	119.4	372.0	0.65	51.4	0 448
560	293.3	30.8	16.1	258.9	118.4	377.3	0.65	51.0	0.482
570	298.9	34.1	19.4	265.4	117.3	382.7	0.66	50.7	0.537
580	304.4	37.7	23.0	272.0	116.1	388.1	0.66	50.3	0.585
590	310.0	41.8	27.1	278.6	115 0	393.6	0.66	49.9	0.637
600	315.6	46.0	31.3	285.2	113.7	398.9	0.66	49.5	0.697
650	343.3	72.6	57.9	318.7	107.4	426.1	0.67	47.6	1.10
700	371.1	109.6	94.9	352.5	99.4	451.9	0.68	45.5	1.67

[a] The Dow Chemical Co., *The Dowtherm Story*. Midland, Mich., 1948.

After deodorization is completed, the oil must be cooled before it is discharged to the atmosphere. Hydrogenated products which are relatively resistant to oxidation may be brought out of the deodorizer at a temperature as high as about 150°F. (66°C.) without appreciable injury to the flavor, but a temperature of 100–120°F. (38–49°C.) is generally preferred for liquid oils. Some processors do not expose deodorized fats or oils to the atmosphere at all, but discharge them to nitrogen-blanketed tanks and fill all packages of the finished product under nitrogen. If the oil is not afforded the protection of an inert gas, it should be packaged as soon as possible, and preferably within a few hours after deodorization, as even the more stable products will deteriorate slightly in flavor upon prolonged holding in storage tanks or upon being repeatedly melted and resolidified.

In batch deodorizers the oil may be cooled either within the deodorizer, by the circulation of water through cooling coils, or externally, as it is pumped through a shell and tube cooler. Cooling is effected within the deodorizer in the so-called semicontinuous apparatus. To facilitate heat exchange, and also to make stripping as thorough as possible, it is ad-

visable to continue steaming at a reduced rate during the cooling or pump-
ing period; during this period full vacuum should be maintained on the
oil. When cooling is conducted wholly within the deodorizer, at 6 mm.
pressure, the temperature may be reduced to 130–150°F., depending upon
the oil depth, before condensation of the stripping steam begins to occur.
The practice of transferring the hot deodorized oil to a separate cooling
tank is not to be recommended, unless the latter is, like the deodorizer,
maintained under high vacuum and provided with stripping steam.

In the continuous deodorization of oils, both heating and cooling are
conducted outside the deodorizer proper, and usually heat exchange is
effected between the incoming and outgoing oil.

(c) Protection of the Oil Against Oxidation

At the high temperatures used for deodorization, reaction of the oil
with atmospheric oxygen is very rapid. As slight oxidation is not only in-
jurious to the stability of the oil, but altogether ruinous to the flavor,
the oil must be protected rigorously from air leakage. Leakage of air into
the hot oil is particularly prone to occur in batch or continuous units
where the hot oil is pumped out of the deodorizer through external coolers
or where the oil is circulated through external heaters. Much poor practice
in deodorization results, not from insufficient stripping, but from allow-
ing air to gain access to the deodorized oil before it is cooled. In welded
vessels leaks in the deodorizer body do not often occur, but very careful
maintenance is required to avoid the development of leaks in fittings be-
low the oil level and in external heaters, coolers, and pumps. Nullification
of the risk of air leakage is one of the chief virtues of the special "double-
wall" construction employed in one type of deodorizer (pages 792–793).

As oil exposed to the atmosphere will dissolve an appreciable amount of
air, an efficient deaerator for the feed oil is an essential adjunct of con-
tinuous apparatus in which the oil is heated before it comes into contact
with stripping steam.

In some plants deodorized fat is never exposed to the atmosphere, but
is kept under an atmosphere of nitrogen from the deodorizer to the pack-
age.

(d) Materials for Deodorizer Construction

Most of the older batch deodorizers now in operation are made of or-
dinary carbon steel. However, at the high temperatures now commonly
used in deodorizing, ordinary steel definitely acts as a pro-oxidant for the
oil; hence in the newer continuous and semicontinuous apparatus, as well
as some batch installations, preference has been given to special metals
or alloys such as nickel or stainless steel.

In a study of deodorization under laboratory conditions, Ziels and Schmidt[22] found that only nickel and aluminum, of a number of materials examined, were wholly without pro-oxidant effect on the oil. Aluminum has thus far found little or no use as a material for deodorizer construction, because of its lack of structural strength at high temperatures and because of the difficulty of cleansing it of films of polymerized oil, but many nickel deodorizers have been built.

(e) Treatment of Stripping Steam

Although it was formerly the general practice to superheat the steam used for stripping in deodorization, many processors now omit superheating. In modern deodorizers, which operate at low pressures and with correspondingly low steam flows, the cooling effect of steam that is not superheated is relatively slight. However, the stripping steam should be dry, and should be substantially free of oxygen.

(f) Recovery of Deodorizer Distillate

The fatty distillate from deodorization consists of free fatty acids, neutral oil, and unsaponifiable matter. In contact with barometric condenser water the free acids react to a considerable extent with calcium carbonate in the water, to form calcium soaps. Newby and Gulino[23] have shown that these consist largely of saturated compounds, as calcium reacts with saturated fatty acids preferentially.

The distilled material appears in the condenser water in the form of small flocs, which rise to the surface of the water and coalesce upon standing. Usually the water is discharged into long catch basins in which the velocity of the stream is slowed sufficiently to allow fatty material to rise to the surface, where it may be skimmed off. The skimmings are heated to separate occluded water, and usually put into soapstock, as their high content of unsaponifiable material and metal soaps and their malodorous nature renders them unsuitable for any other purpose. However, if high in tocopherols, e.g., 3–8%, they may be subjected to processing for tocopherol recovery.

In the upper portions of the apparatus, the vapors leaving the deodorizer are generally cooled sufficiently to precipitate a considerable proportion of the distilled fatty material in the form of a fog. At the low pressures and high vapor velocities employed in deodorizing it is difficult to separate or condense any large proportion of the distillate before it reaches the condensers. However, the separators or "knockout drums" that are frequently placed in the vapor lines to remove mechanically entrained fat

[22] N. W. Ziels and W. H. Schmidt, *Oil & Soap*, **22**, 327–330 (1945).
[23] W. Newby and E. A. Gulino, *J. Am. Oil Chem. Soc.*, **26**, 418–422 (1949)

also act as partial condensers and recover a minor part of the distillate. Neutral fat is condensed more readily than unsaponifiable matter, which is in turn condensed more easily than the fatty acids. If little oil is carried into the separators by entrainment, the material collected there may be relatively high in tocopherols.

2. BATCH DEODORIZATION

Although many odd designs for batch deodorizers are to be found in the patent literature, few of them have found practical use, and substantially all present batch deodorization is carried out in vessels of simple and quite uniform design.

The conventional batch deodorizer is a vessel in the form of a vertical cylinder with dished or cone heads; in modern installations the vessel is invariably welded and well insulated. The usual range of capacity is about 10,000 to 40,000 pounds, with a capacity of about 25,000 pounds being perhaps the most common. Deodorizers are usually designed to hold 8–10 feet of oil, and to have a similar amount of headspace above the surface of the oil; hence a 25,000 pound vessel may be about 8.5 feet in diameter and 17–18 feet high. The stripping steam is injected in the bottom of the vessel through a distributor, which usually consists of a flat "spider" of perforated pipes radiating from a central steam delivery line. A convenient method of controlling the flow of stripping steam is to maintain a fixed pressure back of an orifice of known size. As the steam pressure always falls to a low value beyond the orifice, the flow of steam will be proportional to the absolute pressure on the high side. In addition to the steam ejector system and means for heating, cooling, and pumping the oil, necessary accessories include a thermometer or other device for indicating the temperature of the oil and a pressure gage designed to indicate accurately low pressures within the deodorizer independently of the barometric pressure.

To avoid excessive refluxing, it is desirable to make the vapor line leading from the top of the vessel to the booster or to an entrainment separator as short as possible. In some installations, the top of the deodorizer and the vapor outlet are jacketed and heated.[18] Entrainment separators are sometimes placed in the vapor line; in other installations separators of the centrifugal or "Venetian blind" type are placed in the upper part of the deodorizer proper.

A typical batch deodorizer installation, using internal Dowtherm heating, is shown in Figure 132.

Current practice in batch deodorization in the United States has been reviewed by Bodman et al.,[18a] James,[24] and Morris.[17] With modern

[24] E. M. James, in *Cottonseed and Cottonseed Products.* A. E. Bailey, ed., Interscience, New York, 1948, p. 721.

equipment operating at a high temperature and at 6–12 mm. pressure, about 8 hours is usually allowed for the complete cycle of charging, heat-
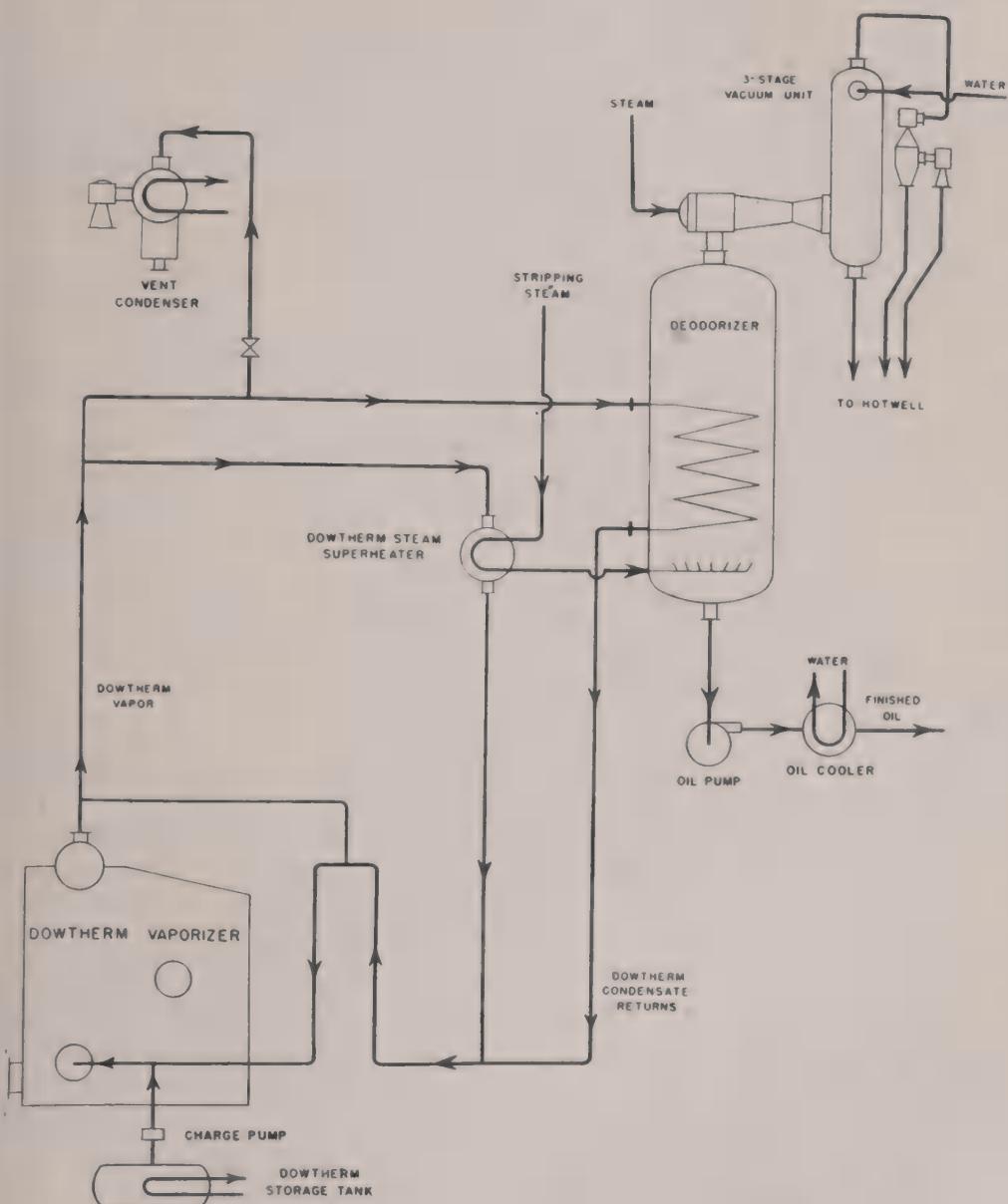
Fig. 132. Batch deodorizing system with internal oil heating and external cooling (courtesy *The Foster Wheeler Corp.*).

ing, deodorizing, and cooling and discharging; this gives a deodorizing time at top temperature of about 4.5 hours. Older installations operating

at a higher pressure and/or a lower temperature may require a time cycle as great as 10–12 hours.[17] Ordinarily, stripping steam is injected at the rate of about 3 pounds per 100 pounds of oil per hour at 6 mm. pressure, with the steaming rate being proportionately greater at higher pressures. The total amount of stripping steam used may vary from about 10 pounds to 50 pounds per 100 pounds of oil; the average is probably about 25 pounds.[24]

The temperatures employed in deodorization vary considerably in different plants. In the United States, hydrogenated vegetable oil stocks are generally deodorized within the range of 400–475°F. (204–246°C.), and occasionally as high as 500°F. Many processors deodorize salad and cooking oils at somewhat lower temperatures than hydrogenated oils. Lard and similar animal fats are considerably easier to deodorize than vegetable oils and require less elevated temperatures, although a relatively high temperature is often used to permit deodorizing and steam refining in one operation (see page 651). On the other hand, very high temperatures, which cause some degree of heat polymerization, are considered desirable for unhardened marine oils.

3. Continuous Deodorization

Although a number of devices for continuous deodorization have been patented, and some have been used to a limited extent abroad, there are apparently not more than four such systems now in active use in the United States.

The oldest of these,[17,18a,25] introduced in about 1936, is illustrated in Figure 133. The deodorizer proper consists of a stainless steel tower fitted with 12 shallow trays with bubble caps, down which the oil flows countercurrent to the stripping steam. The raw oil, after deaeration under vacuum, is heated by exchange with the hot effluent oil, and then by Dowtherm; the finished oil is pumped out of the tower through an oil-to-oil heat exchanger, and then through a cooler, to storage or to a filter. A three-stage steam ejector system maintains a pressure of 6 mm. at the top of the column and 18–22 mm. at the bottom. Operating temperatures are usually in the upper portion of the range quoted above, i.e., about 450–475°F. (232–246°C.), and at rated capacity the nominal retention time of the oil on the trays is about 20 minutes. Stripping steam requirements under the usual operating conditions are 10 pounds per 100 pounds of oil. Standard units have capacities of 2500 and 5000 pounds per hour.

[25] D. K. Dean (to Foster Wheeler Corp.), U. S. Pat. 2,280,896 (1942). D. K. Dean and E. H. Chapin, Oil & Soap, 15, 200–202 (1938). E. H. Chapin and D. K. Dean, ibid., 17, 217–222 (1940).
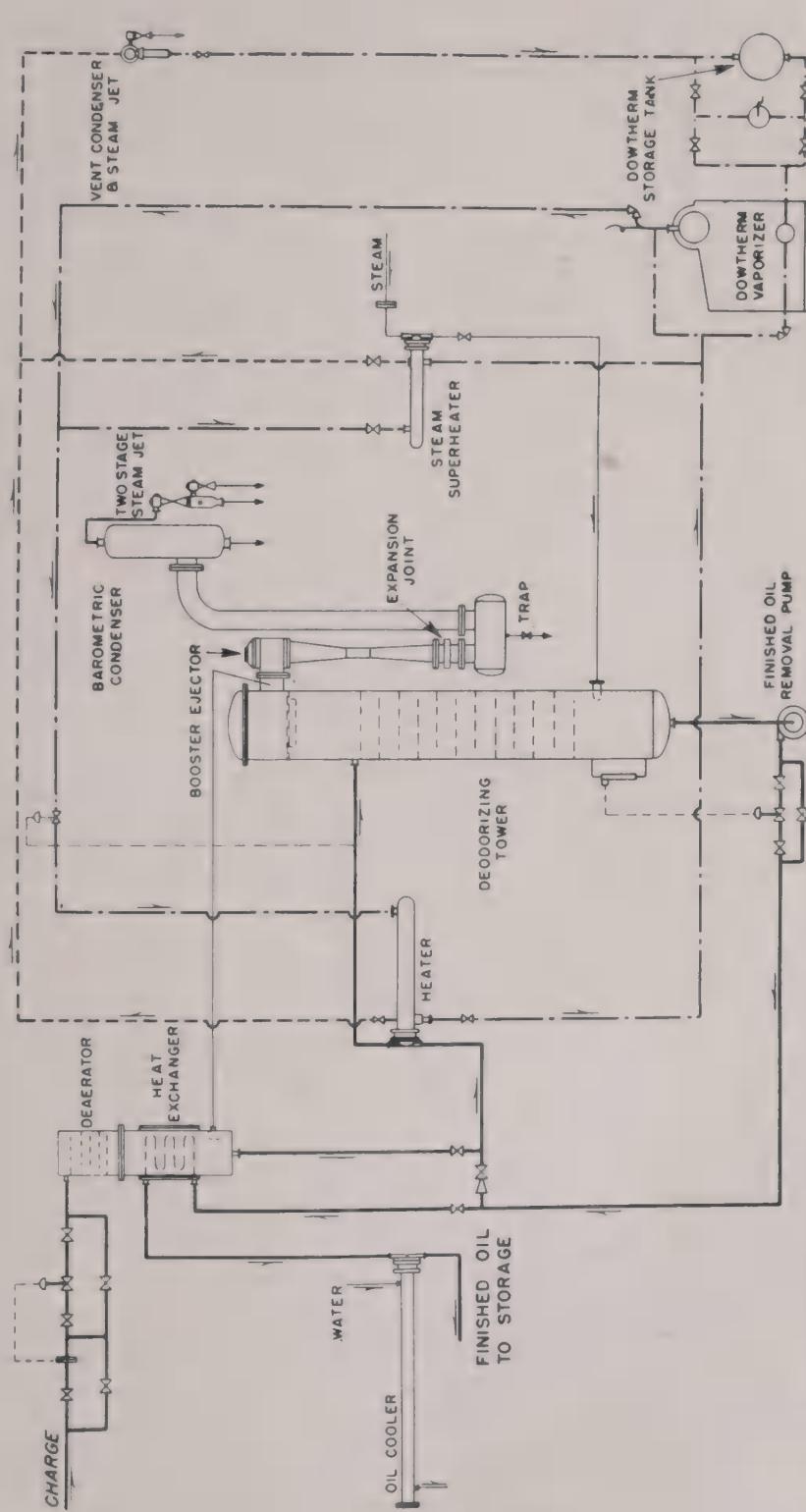
Fig. 133. Continuous deodorizing system with tray and bubble-cap tower (courtesy *The Foster Wheeler Corp.*).

A second deodorizer, [12,18a,26] introduced in 1948, is illustrated in Figure 134. It is termed a "semicontinuous" deodorizer, inasmuch as the oil is deodorized in separate and discrete portions, even though its action is essentially continuous. Successive charges of oil are dropped from a measuring tank into a series of superimposed nickel trays supported within a carbon steel shell, with the oil remaining for one-half hour in each tray. In the top tray the oil is deaerated and heated to approximately 330°F. with steam; in the second tray it is heated to operating temperature (usually 430–480°F. or 221–249°C.) with Dowtherm vapor, in the third and fourth trays it is subjected to stripping (a small amount
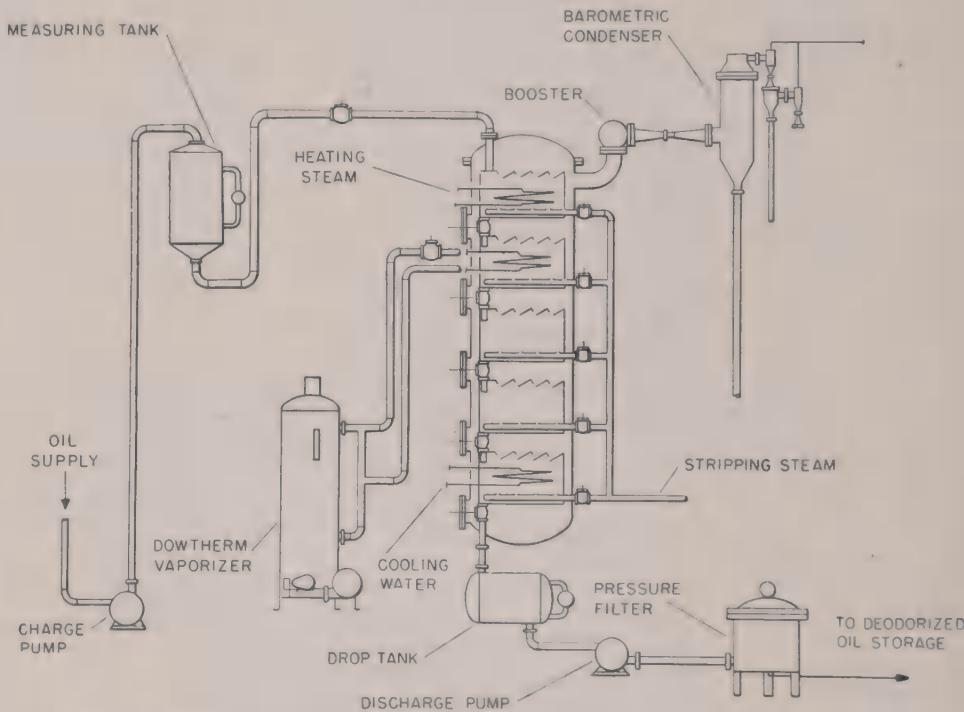
Fig. 134. Semicontinuous deodorizer (courtesy *The Girdler Corp.*).

of steam is also injected into the other trays, for deaeration and agitation); and in the bottom tray it is cooled before it is dumped into a drop tank from which it is continuously pumped through a pressure filter to storage. Operation of the unit is made fully automatic by use of a timing device which opens and closes the various oil valves.

Efficient stripping is attained in the relatively shallow (24-inch) pool of oil in each tray by utilizing the kinetic energy of the expanding stripping steam to splash the oil violently against the under surfaces of a special baffle assembly placed 12 inches above the oil level. An umbrella above the baffle assembly serves to retain particles of oil occasionally

[26] A. E. Bailey, *National Provisioner*, October 30, 1948, pp. 10, 11, 23.

spurting through the baffles and diverts any fatty condensate from the relatively cool shell or vapor outlet into the free space between trays and shell, and thence to the bottom of the shell, where it is recovered in a small shell-drain tank. Since the stripping steam passes out of each tray into the vapor passage next the shell, contact between steam and oil, unlike that in the deodorizer described above, is noncountercurrent, and equal pressures of 6 mm. are maintained on all trays. The semicontinuous deodorizer possesses the advantage over any completely continuous apparatus of great flexibility, *i.e.*, it can be started up or shut down without loss of operating time, and, as all trays and tanks drain cleanly, it can be quickly switched from one oil stock to another without loss of time or
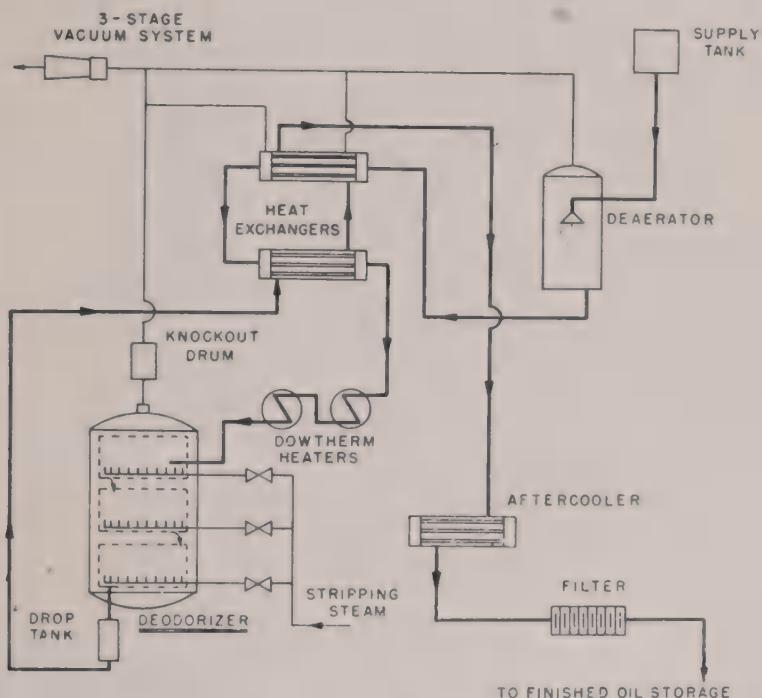
Fig. 135.   Continuous deodorizing system with noncountercurrent flow of steam and oil and separated trays and shell.[27]

without intermixing of the two stocks. The "double-wall" construction of trays within an outer shell renders it impossible for air accidentally leaking into the apparatus to come into contact with the hot oil.

Units of standard size have capacities of 2000, 5000, and 7500 pounds per hour. The stripping steam required is 4.5 pounds per 100 pounds of oil deodorized.

A third continuous deodorization apparatus, first operated in 1949, utilizes an external deaerator of the flash type and a heat-exchange sys-

tem essentially similar to that which is depicted in Figure 133. The general design is shown in Figure 135. The hot feed oil, at a temperature of about 450°F. (232°C.), follows a tortuous path through narrow passageways in three square superimposed nickel trays. A double-wall construction similar to that of the semicontinuous deodorizer is used to avoid air leakage and prevent refluxing, and a similar arrangement of "splash baffles" is relied upon to retain the oil and disperse the oil and steam sufficiently to obtain a high vaporization efficiency in the shallow (9-inch) layer of oil. A pressure of 6 mm. is maintained on the oil by means of conventional three-stage steam ejector equipment. The unit has a rated capacity of 5000 pounds per hour, with a nominal oil retention time of 54 minutes. Stripping steam is used at the rate of 3.0 pounds per 100 pounds of oil.[27]

No information is available on a fourth recently developed deodorizer of the continuous type, which is known to be in successful commercial operation.

[27] W. H. Shearon, Jr., H. E. Seestrom, and J. P. Hughes, *Ind. Eng. Chem.*, *42*, 1266–1278 (1950).

FAT SPLITTING, ESTERIFICATION, AND INTERESTERIFICATION

It is logical to consider together the operations of *fat splitting*, in which fat is hydrolyzed to yield free fatty acids and glycerol, *esterification*, in which the free fatty acids are recombined with glycerol or with another alcohol, and *interesterification*, in which glycerides or other fatty esters are reacted with fatty acids, alcohols, or other esters, to bring about the interchange or redistribution of fatty acid radicals. The different reactions involve similar groups, and are in general responsive to the same catalysts. All involve the migration of fatty acid radicals.

Fat splitting has been extensively practiced for nearly a century, for the production of fatty acids for soapmaking and the manufacture of candles. Esterification and interesterification processes have but recently begun to receive attention, but can be expected to assume increasing importance in the future. These processes are more or less essential tools in the manufacture of the new, so-called "tailor-made" fats and oils, and have other important industrial applications.

A. Composition of Partially Split, Esterified, or Interesterified Fats

There is ample evidence that the migration of fatty acid radicals to or from a glyceryl residue is not to any large degree selective, but is a rather haphazard affair in which all fatty acids in the reacting system participate on a more or less equal basis. Because of this, a partially split or partially esterified fat never consists purely of triglycerides, but always also contains mono- and diglycerides. In the case of esterification or interesterification reactions, if the reactants are permitted to come to equilibrium while free hydroxyl groups are present to allow continued interchange of fatty acid radicals, the esterified fatty acid radicals will tend to be distributed in a random manner among all available sites for esterification, *i.e.*, among all esterifiable hydroxyl groups. In other words, ester–ester or ester–alcohol interchange is to be regarded as a process in which the various fatty acid radicals undergo continual shuffling among the alcoholic hydroxyl groups, and eventually reach a state of random distribution which does not alter as shuffling is continued. As a conse-

quence, it is often possible to calculate the composition of a reaction product from the relative molar proportions of the different reactants. with the aid of equations based upon simple probability considerations. Formulas for such calculations, and examples of their use will be found on pages 834–837. The composition of the product will, of course, be altered, if conditions are such that all of the reactants do not form a single homogeneous phase, or if a reaction product is continuously removed from the sphere of reaction. Actually, the technology of splitting, esterification, and ester interchange is very largely concerned with techniques for the removal of reaction products to permit specific reactions to go largely to completion, or to obtain one desired component of an equilibrium mixture in preponderant amount.

B. Fat Splitting

1. GENERAL CONSIDERATIONS

(a) Composition of Partially Split Fat

The over-all reaction in fat hydrolysis or fat splitting is as follows:

$$
\begin{array}{l}
\text{H} \\
\text{|} \\
\text{H—C—OOC.R}_1 \\
\text{|} \\
\text{H—C—OOC.R}_2 \quad + \quad 3\,\text{HOH} \\
\text{|} \\
\text{H—C—OOC.R}_3 \\
\text{|} \\
\text{H}
\end{array}
\longrightarrow
\begin{array}{l}
\text{H} \\
\text{|} \\
\text{H—C—OH} \qquad \text{HOOC.R}_1 \\
\text{|} \\
\text{H—C—OH} \quad + \quad \text{HOOC.R}_2 \\
\text{|} \\
\text{H—C—OH} \qquad \text{HOOC.R}_3 \\
\text{|} \\
\text{H}
\end{array}
$$

Triglyceride   Water   Glycerol Free fatty acids
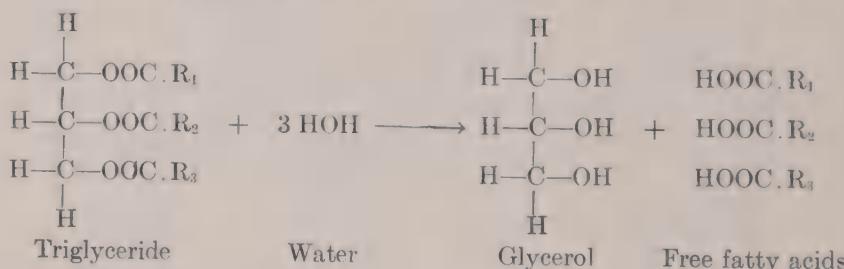
However, the reaction naturally proceeds in stages, with the fatty acid radicals being displaced from the triglyceride molecule one at a time, so that an incompletely split fat will contain both mono- and diglycerides. as well as triglycerides. It was demonstrated by Kellner[1] that the extent to which mono- and diglycerides are formed is considerably variable according to the conditions under which splitting is carried out. Mono- and diglycerides corresponding to as much as 3.5% excess combined glycerol were produced in fat partially split in an autoclave. Less mono- and diglycerides were produced in splitting by the Twitchell method, and still less in fermentative fat splitting. No mono- or diglycerides were produced by partial saponification of a fat with a strong alkali.

Mueller and Holt[2] found that in the Twitchell splitting of coconut oil the proportions of mono-, di-, and triglycerides became constant early in the reaction at ca. 14, 33, and 42% by weight, or 25, 33, and 42 mol per cent, respectively (corresponding to about 18.3% combined glycerol),

[1] J. Kellner. Chem.-Ztg., 33. 453 (1909); 33. 661–662 (1909).
[2] H. H. Mueller and E. K. Holt, J. Am. Oil. Chem. Soc., 25. 305–307 (1948).

and did not change with subsequent change in the free glycerol concentration of the aqueous and fat phases (see Fig. 136). In their study of the autoclave splitting of tallow and coconut oil without a catalyst, Mills and McClain[2a] did not make analyses of the fat phase in terms of mono-, di-, and triglycerides, but they did observe that at equilibrium, with various degrees of splitting, the combined glycerol content of the unsplit fat was constant, at 18.5–20% for tallow and 22–24% for coconut oil. They found also at equilibrium a constant ratio of combined glycerol to free glycerol in the fat phase (*ca.* 1.8 to 1 for tallow and 1.25 to 1 for coconut oil). The tendency noted by Kellner[1] for the combined glycerol con-
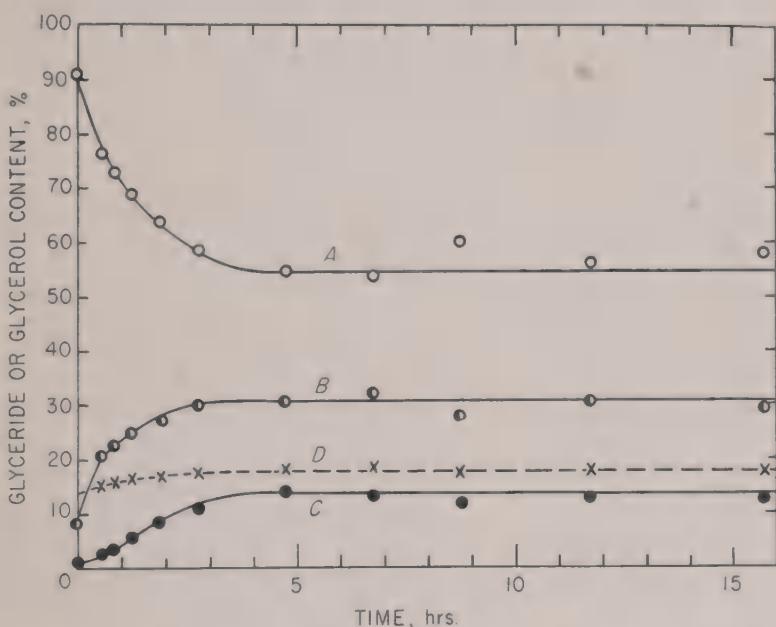
Fig. 136. Composition of unsplit fat during the first boil in the Twitchell splitting of coconut oil: (*A*) triglycerides, (*B*) diglycerides, (*C*) monoglycerides, and (*D*) combined glycerol content.[2]

tent of the unsplit fat to increase with increase in the splitting temperature may be a result of ester interchange among mono-, di-, and triglycerides at the higher temperatures. Actually, in the case of the tallow, the observed content of combined glycerol (18.5–20%) was not very different from that calculated for random distribution at a 1.8 to 1 ratio of combined to free glycerol (*ca.* 20.5%). In the case of the coconut oil, the observed content of combined glycerol was considerably less than that called for by random distribution, assuming equal average molecular weights for the free and combined fatty acids.

[2a] V. Mills and H. K. McClain, *Ind. Eng. Chem.*, *41*, 1982–1985 (1949).

(b) Mechanism of the Reaction

It was first pointed out by Lascaray,[3] and is now generally recognized, that only a minor amount of splitting occurs at the water–fat interface, and that fat splitting is essentially a homogeneous reaction which occurs through the action of water dissolved in the fat phase. Water is much more soluble in fatty acids than in neutral fats; hence a curve representing the degree of splitting as a function of time is sinusoidal in shape (see Fig. 138); the reaction is characterized by an initial period when splitting is slow and limited by the low solubility of water in the fat, a middle period when reaction is relatively rapid, and a final period during which the reaction rate diminishes as equilibrium between fatty acids and liberated glycerol is approached. Splitting is accelerated by increasing the temperature largely because of the increased solubility of water in the fat phase.

(c) Rate of the Reaction

Splitting is accelerated by the presence of mineral acids, certain metal oxides, including particularly zinc and magnesium oxides (which form fat-soluble soaps), and organic compounds of the Twitchell type. These, according to Lascaray,[3a] are effective both because they increase water solubility in the fat and because they activate the dissolved water by the liberation of hydrogen ions. During the greater part of the reaction they function in solution in the fat phase, although in the beginning they may also assist hydrolysis through the promotion of emulsions. The ratio of water to fat has an important bearing upon the length to which hydrolysis may be carried; hence in the last stage the rate of splitting increases with increase in the amount of water in the system. In the first stages, however, the reaction rate is not increased by the presence of large amounts of water.

The following data, due to Lascaray,[3] are roughly indicative of the effect of temperature on fat-splitting. The times required at different temperatures to free 50% of the fatty acids in a tallow subjected to treatment in an autoclave with 60% water and 0.5% sodium hydroxide were approximately as follows:

Temperature, °C.	Time, hours
220	0.5
200	0.9
185	2.2
170	4.2
150	9.0

[3] L. Lascaray, *Seifensieder-Ztg.*, *64*, 122–126 (1937); *Fette u. Seifen*, *46*, 628–632 (1939).

[3a] L. Lascaray, *Ind. Eng. Chem.*, *41*, 786–790 (1949).

(d) Maximum Splitting Obtainable

The fat splitting reaction is reversible, and hence a point of equilibrium between hydrolysis and re-esterification will eventually be reached, unless by some means the liberated glycerol is removed from the sphere of reaction. It has been shown by Mills and McClain[2a] that the completeness of hydrolysis depends upon the concentration of glycerol in the fat phase. This concentration is, in turn, directly proportional to the concentration in the water phase; in the autoclave splitting of fats without a
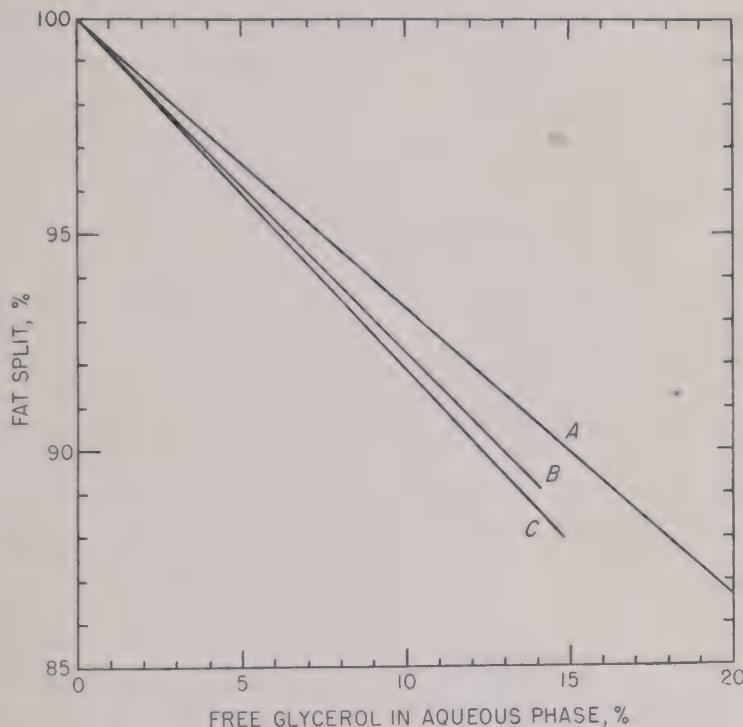
Fig. 137. Maximum hydrolysis in fat splitting as a function of the glycerol content of the aqueous phase: (A) Twitchell splitting of palm kernel oil,[3a] (B) autoclave splitting of tallow,[2a] and (C) autoclave splitting of coconut oil.[2a]

catalyst at 453°F. (234°C.) and 483°F. (251°C.) Mills and McClain found the ratio of free glycerol in the water phase to free glycerol in the fat phase to be 12.5 to 1 for tallow and 7.0 to 1 for coconut oil. Hence, as pointed out previously by Kaufmann and Keller[4] and by Lascaray,[3] the maximum obtainable degree of splitting is a function of the concentration of glycerol in the water; within the range of 80–100% hydrolysis, the relationship between the two is substantially linear. Apparently the

[4] H. P. Kaufmann and M. C. Keller, Fette u. Seifen, 44, 42–47, 105–107 (1937).

relationship between degree of splitting and glycerol concentration is virtually independent of temperature, concentration of water, or the presence or absence of catalysts. The curves of Mills and McClain,[3a] representing complete equilibrium in the autoclave splitting of tallow and coconut oil without a catalyst, and of Lascaray,[3a] representing near equilibrium in the Twitchell splitting of palm kernel oil, are reproduced in Figure 137.

(e) Miscellaneous Characteristics of the Reaction

It has been pointed out by Kaufmann and Keller[4] that the indifference to temperature of the point of equilibrium is an indication of a zero heat of reaction in fat splitting. There is a heat effect, however, associated with the solution of water in the fat phase. In high-temperature splitting, where a large amount of water is dissolved, it is said[4a] that there may be a sufficient absorption of heat to cool the fat 50°F.

In fat splitting, unlike alkali saponification, there is apparently no considerable difference in the reaction rates of saturated and unsaturated fatty acids.[5] In enzymic fat splitting at atmospheric temperatures, according to Sanders,[5a] fatty acids of intermediate chain length, i.e., C_{12} to C_{18}, are liberated most readily, with the ease of splitting tending to decrease as the chain becomes longer or shorter. There appear to be no published data on the effect of chain length on high-temperature fat splitting. In a mixture of polymerized and nonpolymerized glycerides the latter are hydrolyzed preferentially.[6]

2. Twitchell Method

The most commonly employed method of fat splitting depends upon the use of catalytic agents of a type first used and described by Twitchell.[7] The first Twitchell reagents were prepared by sulfonating the reaction product of a fatty acid and benzene or naphthalene. In the case of benzene, the product presumably has the formula $(R) . C_6H_4 . (SO_2OH)$. For commercial use the original Twitchell reagents have been replaced by similar but more active compounds of the Kontakt type, prepared by the sulfonation of petroleum fractions. Stirton et al.[8] have shown that alkyl aryl sulfonic acids derived from certain commercial wetting agents of

[4a] R. C. Daniels (to Procter & Gamble Co.), U. S. Pat. 2,387,884 (1945).
[5] See, for example, G. S. Jamieson and W. F. Baughman, Cotton Oil Press, 7, No. 2, 35–36 (1923); M. Loury, Bull. mat. grasses inst. colonial Marseille, 27, 25–29 (1943).
[5a] J. H. Sanders (to Procter & Gamble Co.), U. S. Pat. 2,485,779 (1949).
[6] R. A. Carleton, U. S. Pat. 2,367,666 (1945).
[7] E. Twitchell, U. S. Pat. 601,603 (1898); J. Am. Chem. Soc., 22, 22–26 (1900).
[8] A. J. Stirton, E. M. Hammaker, S. F. Herb, and E. T. Roe, Oil & Soap, 21, 148–151 (1944).

the alkyl aryl sulfonate type are even more effective splitting agents than the petroleum sulfonic acids.

The Twitchell process has attained much of its popularity as a result of its requiring relatively simple and inexpensive equipment. The operation is carried out in tanks at atmospheric pressure; wooden, lead-lined, or Monel metal tanks are employed, since the process requires some degree of acidity in the aqueous phase. Often the fatty stock to be subjected to Twitchellization contains considerable amounts of albuminous material and other impurities. These have a pronounced poisoning effect on the catalyst,[9] and hence must be removed. It is more or less general practice to subject the fat charge to a period of boiling with dilute sulfuric acid for this purpose before splitting is started. Fat stocks of particularly poor quality are often acid-refined with strong sulfuric acid before they are split.

The acid-washed fat is mixed with about 25–50% of its own weight of water and 0.75–1.25% of its weight of Twitchell reagent. If the fat has not been treated with acid, 0.1–0.2% of strong sulfuric acid is usually added also; this is said[3a] to prevent inactivation of the Twitchell reagent by hard waters. Splitting is carried out by boiling the mixture with open steam over a period of about 36 to 48 hours. The tanks are usually provided with covers, to minimize contact of the charge with air, and consequent excessive darkening of the fatty acids. Even with the most careful operation there is invariably some darkening of the acids. This darkening, the long time required, and the rather high consumption of steam, constitute the chief disadvantages of the Twitchell method.

The splitting is carried out in at least two, and often in three or even four, stages, with the liquor or "sweet waters" containing the liberated glycerol being drawn off at the end of each stage, and replaced with fresh water, or more commonly, with weaker sweet waters from a previous boil, countercurrent operation being maintained throughout the series of boils. Where two periods of boiling are employed, about 85 to 90% of the total splitting will take place in the first stage, and the remainder will take place in the second stage. Typical four-stage operation will distribute splitting in the four stages in the respective proportions of about 60, 25, 10, and 5%. Smaller amounts of water are used if the operation is conducted in a number of stages. The degree of splitting obtained will depend upon the number of stages and the time allotted for the operation; ordinarily about 92–95% of the fat will be hydrolyzed. A higher degree of splitting requires an impracticably long time, and produces excessively weak glycerol solutions.

Although an emulsion is produced during boiling, this will generally break when steaming is discontinued. If a persistent emulsion is formed,

⁹ R. B. Trusler, *J. Oil & Fat Ind.*, **8**, 141–143 (1931).

a little sulfuric acid may be added to break it. The operation is finished by adding fresh water to the fatty acids and boiling to wash out the mineral acid remaining. Some operators recommend the addition of barium carbonate to neutralize the residual sulfuric acid.

3. HIGH-PRESSURE SPLITTING WITH CATALYST

The high-pressure or autoclave method of fat splitting is actually the oldest method employed on a commercial scale; patents covering the process date back as far as 1854. The autoclave method suffered some decline in popularity after the introduction of the Twitchell process, but has lately experienced something of a revival. It is now being used to a considerable extent for splitting higher grade stocks, to produce light-colored fatty acids which do not require distillation. In addition to producing lighter acids, the autoclave process is much more rapid than the Twitchell process.

The catalysts used in autoclave splitting consist of various metallic oxides and hydroxides, of which zinc, magnesium, and calcium oxides are the most commonly used. Of these, zinc oxide is the most active. According to the experiments of Lascaray,[3] different catalysts are decreasingly active in the following order: ZnO, MgO, CaO, LiOH, NaOH, KOH, NH₄OH. About 2–4% of catalyst is used, based on the weight of the fat, and often a fraction of one per cent of zinc dust is also added. The zinc does not act as a catalyst, but through its reducing action, or otherwise, it improves the color of the fatty acids.

The autoclaves are built in the form of tall cylinders, which may be as much as 4 to 6 feet in diameter, and 20 to 40 feet in height. The older autoclaves were usually constructed of copper, but autoclaves are now commonly made from corrosion resistant nickel–chrome alloys. The autoclaves are insulated, and equipped with lines for the injection of steam, but no mechanical agitators.

In operation, the autoclave is charged with the fat, the catalyst, and water equivalent to about 30–60% of the weight of fat. Steam is blown through the mass to displace air in the headspace and dissolved air in the fat and water, and the autoclave is then closed, and steam is admitted to raise the internal pressure to about 150 pounds. The steam is injected at the bottom; condensation of steam within the vessel plus the venting of a small amount of steam maintains a sufficient steam flow to keep the charge agitated. About 6 to 10 hours are required to bring about a splitting of 95%, or better. After the desired degree of splitting is obtained, the contents are blown out into a settling tank, where the separated fatty acids are drawn off from the water–glycerol liquors. The fatty acids must then be treated with sulfuric or other mineral acid, to decompose the soaps formed by the catalyst, after which they are washed free of mineral acid.

There are in the literature virtually no modern data pertaining to the details of autoclave fat splitting, but the above-mentioned laboratory data of Lascaray are of some interest, since they illustrate the relative effect of different factors on the reaction. The effect of temperature and the order of effectiveness of the different catalysts have been mentioned above. In Figure 138 are shown the results of a series of tests carried out at different temperatures on tallow, using 60% of water and 0.5% sodium hydroxide as a catalyst. The same figure also shows the results of a corresponding test at 185°C. in which 0.51% zinc oxide was used as a catalyst, and a test at this temperature without a catalyst.

The temperatures employed in these tests correspond to gage pressures of steam as follows: 140°C., 38 pounds; 170°, 100 pounds; 185°, 148 pounds; 200°, 210 pounds; 220°, 322 pounds.
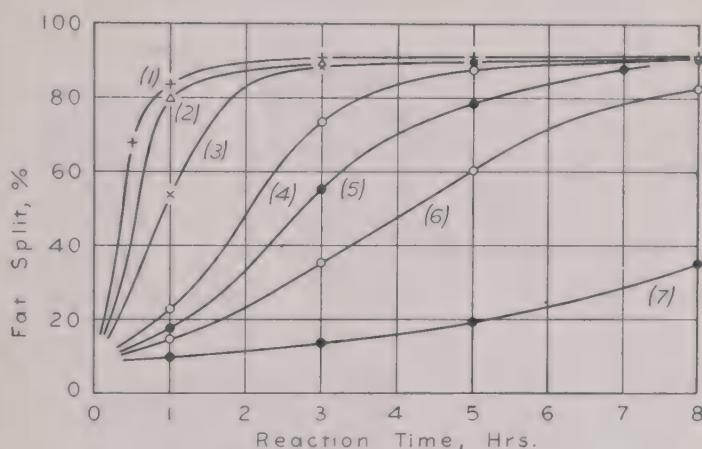
Fig. 138. Autoclave splitting of tallow with 60% water: (1) at 220°C. with 0.5% NaOH as a catalyst; (2) at 185°C., 0.51% ZnO; (3) 200°C., 0.5% NaOH; (4) 185°C., 0.5% NaOH; (5) 185°C., no catalyst; (6) 170°C., 0.5% NaOH; and (7) 140°C., 0.5% NaOH.[3]

Autoclave fat splitting with Twitchell reagents is said to be effective at temperatures below those required with lime, zinc oxide, etc., but the necessity for maintaining the system acid so limits the materials from which the autoclave can be constructed as to render the method more or less impracticable.

4. HIGH-PRESSURE SPLITTING WITHOUT CATALYST

Autoclave fat splitting without the aid of a catalyst is relatively little practiced, although one large American manufacturer is reported to be currently employing this process. By using a special autoclave fabricated from stabilized stainless steel, and equipped with an efficient mechanical

agitator, rapid splitting is said to be accomplished at about 450°F., with the production of light-colored fatty acids, and a very pure glycerol solution.

5. Continuous Splitting

The chief present interest in high-pressure fat splitting is centered on continuous rather than batch processes. One of the new continuous processes, developed by Mills and associates,[10] is discussed in another chapter (Chapter XX) in connection with continuous soap manufacture. Another, the Colgate-Emery process, is described in recent articles by Allen et al.[11] and by Barneby and Brown.[12] It is basically similar to the Mills process, embodying countercurrent flow of water and fat in a splitting tower. Normally, no catalyst is employed, a contact time of 3.5 hours or less being sufficient to produce a split of 97–99%. Temperatures up to about 500°F. are used, and a pressure of 725 pounds per square inch; temperatures as high as 525°F. were found to produce considerable decomposition of glycerol.

In the Colgate-Emery tower the water is described as falling through the fat and fatty acids in the form of fine droplets. Their fall is relatively slow, inasmuch as there is but a very slight difference between the densities of the two phases under operating conditions. Special contacting trays are provided at the top and bottom of the tower, to permit heat exchange and facilitate washing out of dissolved water and dissolved fat from the fatty acids and the sweet water, respectively. Additional heat, to maintain the column at operating temperature, is provided by the direct injection of high-pressure steam.

The ratio of fat to water used is in the range of 1.5–2.0 to 1, and a sweet water containing about 11 to 18% glycerine is produced, depending upon the grade of fat processed. The sweet water requires only a very light lime treatment before concentration to produce a glycerine of exceptionally low ash content. The process is suitable for all animal fats and most vegetable oils, including soybean oil, but appears to cause considerable polymerization in fish oils. For the production of fatty acids of the lightest grades, deaeration of both feedstock and process water is recommended. Untreated water is satisfactory for use in most locations, although demineralization of hard waters is considered advisable.

[10] V. Mills (to Procter & Gamble Co.), U. S. Pat. 2,156,863 (1939). See also N. G. Robisch (to Procter & Gamble Co.), U. S. Pat. 2,267,750 (1941) and R. C. Daniels (to Procter & Gamble Co.), U. S. Pat. 2,387,884 (1945).
[11] H. D. Allen, W. A. Kline, E. A. Lawrence, C. J. Arrowsmith, and C. Marsel. Chem. Eng. Progress, 43, 459–466 (1947). See also M. H. Ittner (to Colgate-Palmolive-Peet Co.). U. S. Pat. Reissue 22,006 (1942).
[12] H. L. Barneby and A. C. Brown, J. Am. Oil Chem. Soc., 25, 95–99 (1948).

The Eisenlohr process[13,14] for continuous fat splitting has found considerable use in the United States. The essential feature of the Eisenlohr apparatus is a long coil of Inconel or other suitable tubing, of small diameter, through which an emulsion of fat and water without catalyst is rapidly pumped while being heated to a very high temperature (*ca.* 600°F.), under a pressure of 3000–3500 pounds per square inch. Splitting takes place rapidly (within about 20 minutes), and partial flashing off of water when the pressure is reduced produces a sweet water very high in glycerol content. Owing, however, to the concurrent flow of fat and water, the degree of splitting is low, amounting to only 85–90%.

6. Enzymic Fat Splitting

Fat-splitting through the use of lipolytic enzymes[15] has been carried out on a commercial scale in the past, although it is doubtful whether this process is of much present importance.

The enzyme preparation is usually obtained from castor beans. The beans are ground with water, and the ground mass is centrifuged to remove solid material. The resulting emulsion of water, oil, protein, etc., is then fermented at room temperature for 48 hours, after which it is ready for use.

Splitting is carried out in open, conical-bottom, lead-lined tanks. The fat is mixed with 30–40% of its weight of water, and about 6% of the ferment. Sufficient acetic acid or other acid is added to bring the pH of the system to a value of about 5, and also manganese sulfate solution equivalent to 0.15–0.20% of the dry salt on the basis of the fat. Barium chloride is also said to be an activator of hydrolysis, whereas mercuric chloride, cupric chloride, silver nitrate, and copper sulfate are inhibitors.[16] A temperature of 35°C. is considered optimum, although reasonably rapid splitting is obtained at temperatures as low as 15°C. or as high as 40°C. Outside this range of temperatures the activity of the ferment falls off rapidly, hence the process is not adaptable to fats of high melting point.

The mass in the tank is agitated, to form an emulsion, and then is held at the proper temperature for about 24 to 48 hours, with occasional stirring. As in other fat-splitting processes, hydrolysis takes place rapidly at first, and then more slowly, eventually reaching a point of equilibrium. About 90% splitting is said to be practicable. After splitting has taken

[13] G. W. Eisenlohr (to M. Werk Co.), U. S. Pat. 2,154,835 (1939). See also M. K. Schwitzer, *Chem. Age, 50,* 601–606 (1944).
[14] C. Marsel and H. D. Allen, *Chem. Eng., 54,* No. 6, 104–108 (1947).
[15] For additional information on enzymatic fat splitting, see E. Schlenker in *Chemie und Technologie der Fette und Fettprodukte.* H. Schönfeld, ed., Vol. II, Springer, Vienna, 1937. pp. 485–491.
[16] M. Loury and J. Max, *Bull. mat. grasses inst. colonial Marseille, 29,* 25–34 (1945).

place, the emulsion is broken by heat and the addition of a little sulfuric
acid, after which the fatty acids may be drawn off and washed, in the
usual way.

7. GLYCERINE RECOVERY AND YIELDS

The sweet waters obtained by Twitchellizing fats are ordinarily neu-
tralized with lime, filtered to remove calcium sulfate; and concentrated
to recover glycerine by the same methods that are used for processing
spent lyes from soap making (pages 859–860). A light treatment with
lime is also said to be desirable for the neutral or nearly neutral sweet
waters resulting from high-pressure splitting without a catalyst.

The maximum theoretical amount of glycerol recoverable from a neutral
fat may be calculated from the saponification value of the latter by the
following formula:

$$\text{Per cent glycerol} = (\text{saponification value})(0.0547)$$

The theoretical glycerol contents of neutral fats and oils of different
saponification values are given in Table 125.

In commercial practice much of the fat split is far from neutral, and
contains from 10 to 50% of free fatty acids. Calculations of glycerine re-
coverable from such fats can readily be made by means of the above
formula, with suitable allowance for the free acid content and for the
content of unsaponifiable material. However, according to Trauth,[17] such
calculated values may be badly in error, from the circumstance that a
large proportion of the glycerides in low-grade, high-acid fats consists
of mono- and diglycerides rather than triglycerides. Trauth, who has
made a careful study of yields in splitting such materials, reports one in-
stance in which the actual yield (from a fat with 58% free fatty acids)
exceeded the calculated yield by 50%, and recommends that glycerine re-
covery be estimated always from actual analysis of the fat for glycerine.

TABLE 125

THEORETICAL GLYCEROL CONTENT OF NEUTRAL FATS AND OILS

Fat or oil	Saponifica-tion value	Glycerol content, %
Tallow, lard, grease, palm oil, cottonseed oil, etc.......	198	10.83
Corn oil, olive oil, peanut oil, soybean oil, sunflower oil, sesame oil, etc..........................	191	10.45
Palm kernel oil...........	248	13.57
Coconut oil......	253	13.84
Rapeseed oil........	175	9.57

[17] J. L. Trauth, *Oil & Soap*, *23*, 137–140 (1946).

C. Esterification

1. Re-esterification of Fatty Acids with Glycerol

The re-esterification of fatty acids and glycerol is exactly the reverse of fat splitting. It is carried out by reacting fatty acids and glycerol at an elevated temperature, while maintaining a vacuum on the reaction vessel or using other means to remove continuously the water which is formed. The reactants are not miscible in all proportions, hence the mixture must be stirred. A partial condenser must be inserted in the vacuum line, to condense and return glycerol vapors to the vessel, while permitting the

TABLE 126

RELATIVE ACTIVITIES OF DIFFERENT INORGANIC ESTERIFICATION CATALYSTS[a,b]

Catalyst	FFA, %	Catalyst	FFA, %
Control, no catalyst....	16.1	NaOH......................	13.8
AlCl$_3$.6H$_2$O..........	17.1	Ni (hydrogenation catalyst)[b]...	16.4
Al$_2$O$_3$[c]	15.4	NiCl$_2$.2H$_2$O................	13.8
CdCl$_2$.2H$_2$O...........	11.0	PbCl$_2$[c]......................	12.0
FeCl$_3$.6H$_2$O...........	11.4	PbO......................	10.9
FeO[c].................	13.9	SbCl$_3$......................	15.0
HgCl$_2$................	15.0	SnCl$_2$.2H$_2$O................	2.8
MgCl$_2$.6H$_2$O..........	13.7	SnCl$_4$.5H$_2$O................	2.4
MgO.................	13.6	SnO$_2$[c]......................	15.1
MnCl$_2$.4H$_2$O..........	13.2	ZnCl$_2$......................	3.5
MnO$_2$...............	10.8	ZnO......................	11.8

[a] From the data of R. O. Feuge, E. A. Kraemer, and A. E. Bailey, *Oil & Soap*, *22*, 202–207 (1945).

[b] Peanut oil fatty acids re-esterified at 200°C. and 20-mm. pressure with an equivalent quantity of glycerol, employing 0.000008 mol of the catalyst per gram fatty acids. Free fatty acid content of the reaction mixtures at the end of 6 hours.

[c] Did not dissolve completely in the reaction mixture.

escape of water vapor. The vessel, like other processing equipment which must come into contact with hot fatty acids, is best constructed of molybdenum stabilized stainless steel, or other resistant alloy, to avoid damage to the vessel through corrosion, and metallic contamination of the product.

Published data on the large-scale re-esterification of fatty acids and glycerol are wholly lacking. However, the reaction has been the subject of some laboratory investigation. It can be considerably accelerated by the use of suitable catalysts. Bhattacharya and Hilditch[18] recommend the use of aromatic sulfonic acids, having been able to effect substantially complete re-esterification in the laboratory at 135–145°C. with 0.5%

[18] R. Bhattacharya and T. P. Hilditch. *Proc. Roy. Soc. London*, *A129*, 468–476 (1930).

naphthalene-β-sulfonic acid as a catalyst. A number of patents specify various heavy metals and metal oxides, including particularly compounds of tin and zinc.[19] Feuge, Kraemer, and Bailey[20] have made a careful laboratory investigation of the esterification of glycerol with an equivalent quantity of mixed peanut oil fatty acids, in the course of which a large number of metal compounds were tested for catalytic activity. The results, summarized in Table 126, show that tin and zinc chlorides are outstanding in activity. (More recently Wocasek and Koch[20a] have reported that zinc fluoride is also a very active esterification catalyst.)

Further study revealed that the reaction, uncatalyzed or catalyzed by most compounds, was bimolecular in character, but that it proceeded in two successive stages, of which the latter had the lower velocity constant and lower energy of activation (10,800 cal. per mol, as compared with 12,300 cal. per mol for the first stage). When catalyzed with either zinc or tin chlorides it was complex and no longer simply bimolecular. Analysis of the reaction mixture indicated the probability that the latter catalysts reacted initially with the free fatty acids and the glycerol to form metallic soaps and chlorohydrins, and that esterification actually resulted from the interaction of these two initial reaction products.

Esterification proceeded at a reasonable rate in a stirred flask under 20 mm. pressure, i.e., the free fatty acid content of the mixture was reduced to 3% in 6 hours, if 0.0008 mol of tin chloride per 100 grams of fatty acids (0.18%) was used at 175°C. (347°F.), or if a similar molar proportion of zinc chloride (0.11%) was used at 200°C. (392°F.). Without a catalyst equally rapid esterification could be obtained only above 250°C. (482°F.). Typical results are shown in Figures 139–141. Neither catalyst appeared to be detrimental to the fat from the standpoint of causing polymerization, conjugation, or undue increase in color, and either could be completely removed by ordinary alkali refining.

To obtain a product consisting of triglycerides, without any substantial content of mono- or diglycerides, it is necessary to maintain a slight excess of fatty acids in the reaction mixture. However, the esterified product need contain no more than 1–2% of free acids.

A patent covering the vapor-phase esterification of fatty acids and glycerol has been issued to German inventors.[21] The operation is conducted in a specially designed apparatus, at a temperature of 220–230°C., and a pressure of 20–100 mm. Condensation of the relatively nonvolatile glycerides serves to remove these from the reaction zone as rapidly as they are formed. Zinc and magnesium oxide catalysts are employed.

[19] F. Gruber, Fr. Pat. 677,711 (1929). I. G. Farbenindustrie A.-G., Fr. Pat. 654,535 (1928), Ger. Pats. 514,403 and 556,558 (1930). J. Y. Johnson, Brit. Pat. 302,411 (1928).
[20] R. O. Feuge, E. A. Kraemer, and A. E. Bailey, Oil & Soap, 22, 202–207 (1945).
[20a] J. J. Wocasek and J. R. Koch, J. Am. Oil Chem. Soc., 25, 335–337 (1948).
[21] I. G. Farbenindustrie A.-G., Ger. Pat. 565,477 (1932).
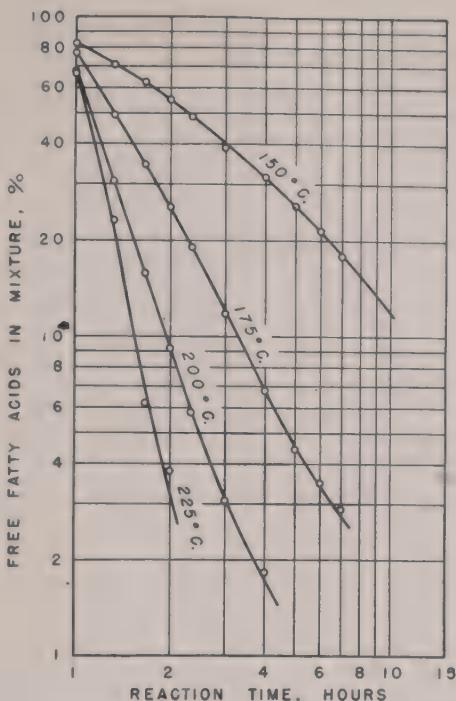
Fig. 139. Re-esterification of peanut oil fatty acids with an
equivalent quantity of glycerol without a catalyst.[20]
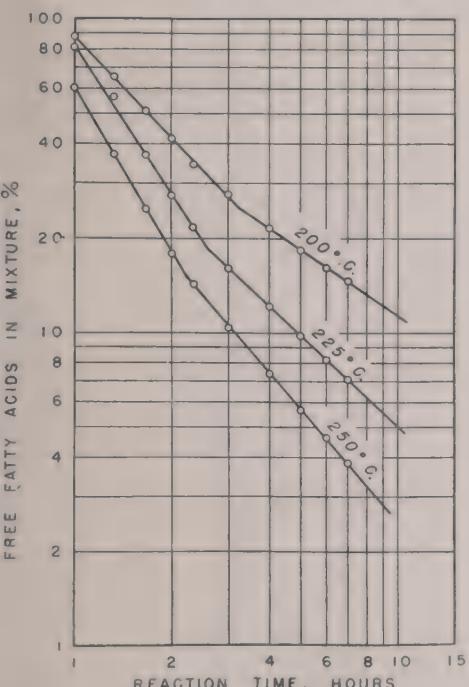
Fig. 140. Re-esterification of peanut
oil fatty acids with an equivalent quan-
tity of glycerol and 0.18% SnCl₂2H₂O
as a catalyst.[20]
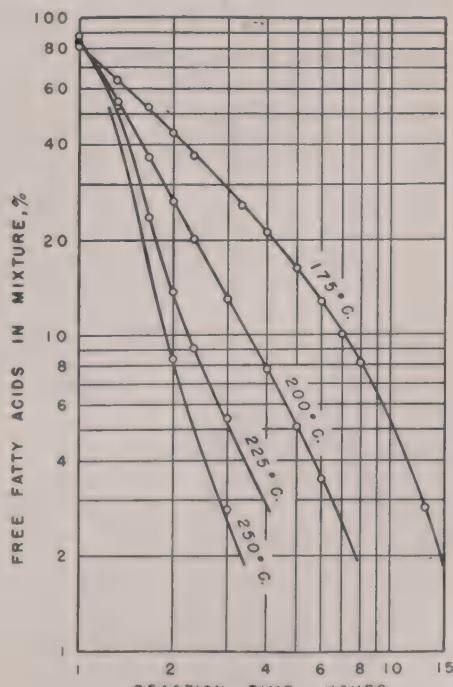
Fig. 141. Re-esterification of peanut
oil fatty acids with an equivalent quan-
tity of glycerol and 0.11% ZnCl₂ as a
catalyst.[20]

According to Toyama and co-workers,[22] the rate at which glycerol esterifies with fatty acids is little dependent upon either the chain length or degree of unsaturation of the latter, even esterification having been observed in mixtures of oleic, stearic, and lauric acids. However, Bhattacharya and Hilditch[18] report that lauric acid is esterified with substantially greater ease than stearic or other C_{18} acids. No appreciable difference was noted between stearic and palmitic acids. It may be mentioned that Sudborough and Gittins[23] observed that the rate of acid-catalyzed esterification of methanol with saturated fatty acids was nearly independent of chain length in the range of butyric to stearic (C_4 to C_{18}), and that Thomas and Sudborough,[24] from another study of esterification with monohydric alcohols, reported that the presence of a double bond had little effect upon the esterification rate, provided that it was two carbon atoms or more removed from the carboxyl group.

2. ESTERIFICATION WITH OTHER POLYHYDRIC ALCOHOLS

The kinetics of the esterification of diethylene glycol with an equivalent proportion of caproic acid at 166°C. were investigated by Flory,[25] who observed that the reaction, in its later stages, had the characteristics of a reaction of the third order, i.e., there was a linear relationship between the reaction time and the *square* of the concentration of carboxyl groups unreacted, rather than the first power of the latter concentration, as in a bimolecular or second-order reaction. This was attributed to the esterification, like that with monohydric alcohols, being catalyzed by hydrogen ions, so that the reaction rate was proportional to the concentration of free hydroxyl groups and to the square of the concentration of free carboxyl groups. Similar characteristics were exhibited by the reaction of lauric acid with lauryl alcohol, as well as certain similar reactions.

There is much present interest in the esterification of unsaturated fatty acids with pentaerythritol and other polyhydric alcohols containing more hydroxyl groups than glycerol, because of the utility of the esters in quick-drying protective coatings (see pages 436–437). Blagonravova and Lazarev[26] have reported that pentaerythritol is readily esterified with oleic or linoleic acids at 200–240°C. (392–464°F.) without the assistance

[22] Y. Toyama, T. Ishikawa, and G. Akiyama, *J. Soc. Chem. Ind. Japan.*, 37, 193–195 (1934).
[23] J. J. Sudborough and J. M. Gittins, *J. Chem. Soc.*, 93, 210–217 (1908).
[24] E. R. Thomas and J. J. Sudborough, *J. Chem. Soc.*, 101, 317–328 (1912).
[25] P. J. Flory, *J. Am. Chem. Soc.*, 61, 3334–3340 (1939).
[26] A. A. Blagonravova and A. M. Lazarev, *J. Applied Chem. U.S.S.R.*, 13, 879–883 (1940).

of a catalyst, and with no appreciable occurrence of oxidation or poly-merization. With equivalent proportions of the reactants the reaction was found to be strictly bimolecular; the calculated energy of activation, 10,652 cal. per mol, was close to that observed by others for the energy of activation in the esterification of fatty acids with glycerol or mono-hydric alcohols. The two unsaturated acids esterified with equal readiness.

Burrell,[27] as a result of considerable laboratory and pilot plant experi-ence, has recommended that pentaerythritol esterification be carried out at 200–230°C. (392–446°F.) in a vessel equipped with an agitator de-signed to lift the heavy alcohol from the bottom of the reaction mixture. For low-acid products an excess of 2–3% of the alcohol is used. Azeotropic distillation with a high-boiling hydrocarbon, *e.g.*, tri-isopropylbenzene, is suggested as an alternative to operation under reduced pressure, for the removal of water liberated by the reaction. As an effective catalyst, cal-cium naphthenate[28] is particularly recommended, along with calcium stearate and limed rosin. Various other metal salts[27] are catalytically active, as are litharge and sulfuric or aromatic sulfonic acids, but these are inclined to produce dark-colored products. Apparently an acid value of 8–10 (4–5% free fatty acids) was generally sought in Burrell's work.

Konen, Clocker, and Cox[29] concluded from laboratory work that no available catalyst was sufficiently active and sufficiently free from delete-rious effect on color to justify its use in esterification with pentaerythritol or similar polyhydric alcohols. A number of catalysts increased the initial reaction rate, but could be observed to have little or no effect on the time required to reach low acid values of 2–5 (1–2.5% free fatty acids). To avoid excessive heat bodying they recommend a maximum reaction tem-perature of 450°F., with 5% excess alcohol, and removal of water by stripping with an inert gas.

Mueller and co-workers[29a] have reported that neither lead oxide nor stannous chloride has any appreciable effect upon the rate at which tall oil reacts with glycerol, pentaerythritol, or sorbitol.

The esterification of fatty acids with the higher polyhydric alcohols, such as sorbitol or mannitol, is relatively involved partly because of the ease with which the esters polymerize, and partly because of the marked tendency of free hydroxyl groups of the alcohols to interact, with the loss of water and the production of ethers. Konen *et al.*,[30] using a ratio of 4 mols of mixed linseed oil fatty acids to 1 mol of sorbitol, and operating at

[27] H. Burrell, *Oil & Soap, 21,* 206–211 (1944).
[28] H. Burrell (to Heyden Chemical Corp.), U. S. Pat. 2,360,393 (1944).
[29] H. Burrell (to Heyden Chemical Corp.), U. S. Pat. 2,360,394 (1944).
[29a] E. R. Mueller, P. L. Enness, and E. E. McSweeney, *Ind. Eng. Chem., 42,* 1532–1536 (1950).
[30] J. C. Konen, E. T. Clocker, and R. P. Cox, *Oil & Soap, 22,* 57–60 (1945).

450°F. without a catalyst, were able to obtain an esterified product with an acid value of 22 in 8 hours and an acid value of 10 in 20 hours. The viscosity was 1.5–2.0 poises, indicating very little polymerization. It was found to be impossible to obtain a low acid value with a higher ratio of fatty acids to alcohol.

Brandner and co-workers,[31] from an extensive series of laboratory experiments, concluded that a molar fatty acid–sorbitol ratio of 4.5 to 1 was optimum for the production of varnish oils from linseed oil fatty acids. Calcium and barium acetates, carbonates, oxides, and hydroxides were found to be the most effective catalysts, 0.5% of mixed calcium and barium acetates (ratio, 3 to 1) serving approximately to double the esterification rate, and produce esters with acid values of 15–20 in the course of 2–4 hours at 180–200°C. (356–392°F.), plus 8–12 hours at 250°C. (482°F.). Considerable bodying occurred at the latter temperature. In all cases it was impossible to attain complete esterification of the hydroxyl groups, regardless of the excess of fatty acids employed, and a check of the amount of water evolved indicated considerable ether formation. The reaction was complex, but over an intermediate range of esterification had approximately the character of a reaction of the first order.

From the work quoted above it is evident that the ease with which a polyhydric alcohol can be esterified is determined largely by its relative proportions of primary and secondary hydroxyl groups, with the latter contributing to nonreactivity. Thus, Konen et al.[30] rate dipentaerythritol, pentaerythritol, glycerol, and sorbitol in order with respect to ease of esterification, while Burrell[29] observed that pentaerythritol is more readily esterified than erythritol, and that trimethylolpropane, pentaerythritol, and glycerol are to be placed in the order named.

3. Esterification with Monohydric Alcohols

The esterification of fatty acids with methyl, ethyl, and other polyhydric alcohols—which is commonly acid catalyzed—is well covered elsewhere,[32,33] and will not be treated here. It may be mentioned, however, that alcoholysis of a neutral fat (page 815) is usually more convenient for the commercial production of monoesters than is esterification of the free acids.

4. Neutralization by Esterification

It has been proposed to effect the neutralization of crude oils high in free fatty acid content by combining the free acids with glycerol to pro-

[31] J. D. Brandner, R. H. Hunter, M. D. Brewster, and R. E. Bonner, *Ind. Eng. Chem.*, *37*, 809–812 (1945).
[32] K. S. Markley, *Fatty Acids*. Interscience, New York, 1947, pp. 254–270.
[33] A. W. Ralston, *Fatty Acids and Their Derivatives*. Wiley, New York, 1948. pp. 492–498.

duce neutral glycerides, rather than by removal of the free acids. A number of patents have been issued covering the process. As an alternative to esterification with free glycerol, the oil may be reacted with mono- and diglycerides.[33a] As a practical means of carrying out neutralization by esterification, it is recommended[33b] that the amount of glycerol be so restricted as to leave a small residue of free acids at the end of the reaction, and that this residue be removed by steam refining.

D. Interesterification

As used here, the term "interesterification" refers to that class of reactions in which a fat or other material composed of fatty acid esters is caused to react with fatty acids, alcohols, or other esters, with the interchange of fatty acid groups.

1. INTERCHANGE BETWEEN A FAT AND FREE FATTY ACIDS

Under the proper conditions for reaction a mixture of fat and free fatty acids can in some cases be made to interchange fatty acid radicals. Most of the reported data on this reaction pertain to the introduction of acids of low molecular weight into a fat made up of higher fatty acids. Normann[34] was able to effect partial replacement of the fatty acids in triglycerides with butyric acid by simply heating the mixture without a catalyst. Schwartz[35] has reacted formic, acetic, or propionic acids with neutral coconut oil at 150–170°C. in the presence of sulfuric acid as a catalyst, to produce a stable, low-melting plasticizer for pyroxylin.

Fatty acids of high molecular weight can also be made to displace lower molecular weight acids, though perhaps less readily. According to a patent issued to Barsky,[36] a fat containing low molecular weight acids, such as coconut oil or butterfat, is reacted with about one-fourth to one-half its weight of high molecular weight acids, such as those from cottonseed or palm oil, at 260° to 300°C., without a catalyst, for 2 to 3 hours, and is finally distilled under reduced pressure until the free acids are substantially removed. In the examples quoted, the saponification value of coconut oil was reduced from 258 to 245 by reaction with cottonseed oil fatty acids, and the saponification value of butterfat was reduced from 227 to 212 by reaction with palm oil fatty acids.

A somewhat easier method than any of the above for incorporating any free acid into a fat is that proposed by Grün,[37] wherein the fat is first

[33a] E. R. Bolton and E. J. Lush (to Technical Research Works Ltd.), U. S. Pat. 1,419,109 (1922).
[33b] E. Wecker, U. S. Pat. 1,758,634 (1930).
[34] W. Normann, *Chem. Umschau, 30,* 250–251 (1923).
[35] G. L. Schwartz (to E. I. du Pont de Nemours & Co.), U. S. Pat. 1,558,299 (1925).
[36] G. Barsky (to Wecoline Products, Inc.), U. S. Pat. 2,182,332 (1939).
[37] A. Grün. U. S. Pat. 1,505,560 (1924).

reacted with glycerol, to produce mono- and diglycerides having free hydroxyl groups (see page 819), and these groups are then esterified with the free acid. According to Grün, the entire process can be conveniently conducted at 225–230°C. in a stirred and evacuated vessel in the presence of a catalyst, *e.g.*, 5% of metallic tin or zinc, and the reactions of glycerolysis and esterification can be carried out either successively or concurrently.

As in simple esterification, there should be free acid in excess in the reaction mixture at the conclusion of any of the preceding reactions, and the excess may be removed by either neutralization with alkali or distillation with steam under reduced pressure if a neutral product is desired.

In all of the foregoing processes of free acid interchange or acidolysis the operator has but limited control over the composition of the final product. Because of the random manner in which interchange of fatty acid radicals occurs any specific acid will distribute itself impartially between the esterified and free acid portions. Eckey,[38] has recently patented a method whereby acids of high molecular weight may be incorporated in the esterified product preferentially, leaving the free acids predominantly those of lower molecular weight. It involves operating at subatmospheric pressure in a vessel equipped with a fractionating column, through which acids of lower molecular weight are continuously removed with the aid of a current of stripping steam as they are freed during the course of the reaction. Aluminum, magnesium, or tin soaps, or preferably zinc soaps, are recommended as catalysts; in practice it is convenient to add the metals to the reaction mixture in the form of metal oxides, to the amount of about 0.10–0.25%.

The Eckey process is applicable either for introducing new acids into a fat or for altering the composition of a single fat by reduction of its content of lower molecular weight acids. In an example given in the patent specification 300 parts of palm oil were reacted with 350 parts of mixed palm oil fatty acids and 1.2 parts (0.18%) of zinc oxide at 280–290°C. and 60 mm. pressure for 2 hours, while blowing with steam at the rate of 4.5% per hour. Acids amounting to about 34% of the charge, and consisting largely of palmitic acid (iodine value, 2.5) were distilled out. The residue of glycerides, which contained 26% free fatty acids, was alkali-refined, after which it had an iodine value of 75.8 and a cloud point of 59.3°F., as compared with an iodine value of 49.6 and a cloud point of 84.6°F. for the original (refined) oil.

A similar alteration in the composition of a fat can be brought about[39] by substituting monoesters for the free acid, and using vapors of the cor-

[38] E. W. Eckey (to Procter & Gamble Co.), U. S. Pat. 2,378,006 (1945).
[39] E. W. Eckey (to Procter & Gamble Co.), U. S. Pat. 2,378,007 (1945).

responding monohydric alcohol as a stripping medium. An alkali metal alkoxide of the alcohol is particularly effective as a catalyst for this reaction, although the metal soaps mentioned above may also be used. A recently issued British patent[40] describes a somewhat different way of achieving the same result. The fat, at 250–300°C. and 20–40 mm. pressure, is treated with vapors of the lower alkyl esters of fatty acids of high molecular weight, to displace low molecular weight acids which are continuously removed.

2. INTERCHANGE BETWEEN A FAT AND A FREE ALCOHOL

The interchange of fatty acids between a fat and a free alcohol, or alcoholysis, is analogous to the reaction of acidolysis, described above. Whereas in acidolysis there is an excess of carboxyl groups in the reaction mixture, to which available hydroxyl groups are redistributed, in alcoholysis there is an excess of hydroxyl groups, to which available carboxyl groups are redistributed. The redistribution, as in acidolysis, is wholly random, unless one or more of the reaction products is removed from the sphere of reaction as it is formed. Alcoholysis of triglycerides, then, will normally produce not only free glycerol and triglycerides of altered or rearranged structure, but also mono- and diglycerides,[41–43] as well as esters of the new alcohol, and also partial esters of this alcohol, if it happens to be polyhydric. In a homogeneous reaction mixture, with the proportions of the reactants known, the composition of the mixture at equilibrium can be calculated from probability considerations.[44,45] Often, however, the reaction is carried to substantially complete interchange of the two alcohols, by removing the originally esterified alcohol from the reaction zone as rapidly as it is set free.

The alcoholysis of fats is important commercially, inasmuch as it offers a means of preparing fatty esters other than glycerides, which is often more suitable and convenient than the alternative method of splitting the fats and re-esterifying with the alcohol in question.

(a) Alcoholysis to Produce Monoesters

The alcoholysis of a fat with a monohydric aliphatic alcohol of low molecular weight, such as methanol or ethanol, is catalyzed by both acids and alkalies. The reaction takes place readily at low temperatures;

[40] Lever Bros. and Unilever Ltd., Brit. Pat. 590,951 (1947). See also W. J. Paterson (to Lever Bros. Co.), U. S. Pat. 2,521,742 (1950).
[41] A. Grün, F. Wittka, and E. Kunze, *Chem. Umschau*, *24*, 15–16, 31–34 (1917). A. Grün, F. Wittka, and J. Scholze, *Ber.*, *B54*, 290–299 (1921).
[42] G. K. Rowe, *J. Soc. Chem. Ind.*, *52*, 49–52T (1933).
[43] Y. Toyama and T. Tsuchiya, *J. Soc. Chem. Ind. Japan*, *36*, 232–233B (1933).
[44] R. O. Feuge and A. E. Bailey, *Oil & Soap*, *23*, 259–264 (1946).
[45] R. O. Feuge and A. Gros, *J. Am. Oil Chem. Soc.*, *26*, 97–102 (1949).

Toyama and co-workers[46] demonstrated, for example, that in the presence of sodium hydroxide methanol or ethanol reached an equilibrium with fats at room temperatures within two hours. Hence in this particular process the problem is actually not one of bringing about reaction rapidly, but rather of removing the freed glycerol from the system so that the reaction may proceed to complete or nearly complete conversion of the fat to monoesters.

Displacement of the glycerol in a fat by a low molecular weight alcohol, such as methyl or ethyl alcohol, is readily accomplished on a large scale by the method described by Bradshaw and Meuly.[47]   The process is remarkable not only for producing methyl or ethyl esters directly from the fat, without the intervening step of hydrolysis, but also for taking place at low temperatures, and requiring no alloy steel or other special corrosion-resistant equipment. Where methyl alcohol is used, the reaction is as follows:

$$C_3H_5(R)_3 + 3\ CH_3OH \longrightarrow C_3H_5(OH)_3 + 3\ CH_3R$$

| Fat | Methyl alcohol | | Glycerol | Methyl esters |

The reaction is carried out in any convenient open tank, which may be constructed from ordinary carbon steel. The fat must be clean, dry, and substantially neutral. It is heated to about 80°C. (176°F.), and to it is added commercial anhydrous (99.7%) methyl alcohol in which is dissolved 0.1–0.5% caustic soda or caustic potash. The amount of alcohol recommended is about 1.6 times that theoretically required for the reaction, although the alcohol may be reduced to as little as 1.2 times the theoretical, if the operation is carried out in three steps. Alcohol amounting to more than 1.75 times the theoretical quantity does not materially accelerate the reaction, and interferes with subsequent gravity separation of the glycerol.

After the addition of the alcohol, the mixture is stirred for a few minutes, and is then allowed to stand. The glycerol begins to separate almost immediately; since it is virtually anhydrous and much heavier than the other liquids, it readily settles to form a layer at the bottom of the tank. Conversion of the oil to methyl esters is usually 98% complete at the end of an hour.

The lower layer of glycerol contains not less than 90% of the glycerol originally present in the fat; the upper layer consists of the methyl esters, most of the unreacted alcohol and alkali, the remainder of the glycerol, and a very small amount of soap. These various impurities are removed

[46] Y. Toyama, T. Tsuchiya, and T. Ishikawa, J. Soc. Chem. Ind. Japan, 36, 230–232B (1933).
[47] G. B. Bradshaw and W. C. Meuly (to E. I. du Pont de Nemours & Co.), U. S. Pats. 2,271,619 (1942) and 2,360,844 (1944). See also G. B. Bradshaw, Soap & Sanit. Chemicals, 18, No. 5, 23–24, 69–70 (1942).

from the esters by successive washes with small amounts of warm water.

The Bradshaw patent contemplates use of the methyl esters to make anhydrous soap by a continuous process. The esters are easily saponified by caustic soda or caustic potash at a low temperature, and the methyl alcohol set free, being volatile, is readily recovered for re-use. It would appear, however, that the process may also constitute a valuable means of obtaining mono esters for fractionation to produce "tailor-made" fats and oils. The methyl and ethyl esters of fatty acids are fluid, and relatively stable, noncorrosive, and low boiling and hence are to be preferred to the free acids, particularly where fractionation must be carried out at an elevated temperature, as by distillation.

A recently issued series of patents[48] describes various continuous means for conducting the alcoholysis of fats with lower alcohols and other alcohols, and of separating and purifying the reaction products.

In a recent review by Wright et al.[49] the proper conditions for alcoholysis of fats with methyl and ethyl alcohols are considered in detail, and experiments are also reported on alcoholysis with other monohydric alcohols. It is pointed out that the above-described alkali-catalyzed alcoholysis method is completely successful only if the fat is almost devoid of free fatty acids and the reaction mixture is substantially anhydrous. Failure to comply with either of these conditions tends to cause soap formation, which leads to a loss of alkalinity and also the building up of a gel structure which prevents or retards separation and settling of the glycerol. In ethanolysis difficulty may be anticipated if the free fatty acid content of the oil exceeds about 0.5%. When 30 parts of ethyl alcohol, 100 parts of cottonseed oil, and 0.5% sodium hydroxide were reacted, the yield of glycerol was appreciably lowered by as little as 0.3% water in the reaction mixture. However, the effect of moisture may be partially compensated by the use of additional alkali and/or alcohol. The water tolerance of the above mixture is increased to 0.5–0.6% if the amount of catalyst is doubled or the amount of alcohol is increased to 40 parts, or to at least 0.8% if both catalyst and alcohol are so increased.

It was demonstrated by Wright and co-workers that the rate of the over-all reaction was limited principally by time required for gravity separation of glycerol, inasmuch as continuous centrifugal separation at 65°C. with a holding time of only 5 minutes gave a fairly good yield of glycerol (about 85% of the theoretical). The claim of Bradshaw and

[48] H. D. Allen and W. A. Kline, U. S. Pat. 2,383,579; C. J. Arrowsmith and J. Ross, U. S. Pats 2,383,580 and 2,383,581; E. E. Dreger, U. S. Pat. 2,383,596; G. A. Glossop, U. S. Pat. 2,383,599; J. H. Percy, U. S. Pat. 2,383,614; W. R. Trent, U. S. Pats. 2,383,632 and 2,383,633; all issued in 1945 and assigned to Colgate-Palmolive-Peet Co.

[49] H. J. Wright, J. B. Segur, H. V. Clark, S. K. Coburn, E. E. Langdon, and R. N. DuPuis, Oil & Soap, 21, 145–148 (1944).

Meuly that less alcohol was required by stepwise addition and separation of glycerol was confirmed in the case of methanolysis, but not in that of ethanolysis, where this method caused gel formation. Acid catalysis of the reaction was found unsuitable, owing to the large excesses of alcohol required. Although propyl alcohol was found to be less reactive than the lower alcohols, good results could be obtained by using large excesses. Higher alcohols, including isopropyl alcohol and also furfuryl alcohol and methyl, ethyl, and benzyl Cellosolves, gave unsatisfactory results.

The interesterification of peanut oil with ethanol has been studied in detail by Feuge and Gros,[45] who state that the optimum temperature for the reaction is in the neighborhood of 50°C. (122°F.). A higher yield of free glycerol was obtained at this temperature than at either 30°C. (86°F.) or 70°C. (158°F.).

The reverse of the above reaction, in which methyl or other low molecular weight alcohol is displaced from its fatty acid esters by glycerol, to yield triglycerides and free alcohol, is less easily carried out, but may be accomplished by virtue of the greater volatility of the lower alcohols, as compared with glycerol. The methyl esters are reacted with glycerol, and sodium hydroxide, lead soap, or other catalyst, at a high temperature with stirring, under reduced pressure. The methyl alcohol gradually distills off, leaving the fatty acids combined with the glycerol.

Wright and co-workers[49] carried out experiments in which pentaerythritol was similarly used to displace methyl alcohol from the methyl esters of mixed linseed oil fatty acids. Products with acid values of 4–8 were obtained after 1–4 hours reaction at 225–280°C. and atmospheric pressure with the use of 1% lead as a catalyst, added in the form of the naphthenate. Pentaerythritol, mannitol, sorbitol, etc., were successfully used for the alcoholysis of glycerides, with the liberated glycerol being distilled off under reduced pressure through a partial condenser with the assistance of stripping steam. Methyl esters of fatty acids were also alcoholyzed with furfuryl and other higher monohydric alcohols.

(b) Alcoholysis of Triglycerides with a Higher Polyhydric Alcohol

The displacement of combined glycerol in an oil with another polyhydric alcohol is chiefly of interest as a means of converting drying oils to materials of higher functionality (see page 436) and enhanced capacity for polymerization and quick and hard drying.

Pentaerythritol has been reacted with neutral oils by Blagonravova[50] and others to produce a mixture of the partial esters of pentaerythritol

[50] A. A. Blagonravova, M. A. Antipova, O. N. Savvina, and E. M. Svetlichnaya J. Applied Chem. U.S.S.R., 14, 192–197 (1941).

and glycerol, suitable for further reaction with alkyd resins, etc. Sodium or calcium hydroxide to the amount of *ca.* 0.1% was used as a catalyst, with the reaction being conducted at 220°C. for 2–6 hours. At this temperature it was necessary to avoid having a large excess of pentaerythritol in the reaction mixture at any one time, to avoid decomposition and carbonization of this alcohol. Burrell[27] reports that a much more effective catalyst for the reaction is calcium naphthenate. As little as 0.005% permitted alkali-refined linseed oil to take up 5% of its own weight of pentaerythritol in 15 minutes at 250°C., and with 1.0% the reaction was completed in a few minutes at 230°C. Lead and cerium naphthenates were also active, though tending to produce discoloration of the oil. These catalysts were found to be effective only with primary alcohols. Secondary alcohols, including glycerol, did not respond to their action.

Wright *et al.*[49] have pointed out that the alcoholysis of glycerides with a high-boiling alcohol, such as pentaerythritol, mannitol, sorbitol, methyl and ethyl glucosides, polyglycerols, etc., may be carried to the point of substantial elimination of the glycerol if the reaction is carried out under conditions which make the latter volatile. It is recommended that the oil be heated to 200–250°C. with 1.0–1.5 equivalents of the alcohol plus 0.5–2.0% of a catalyst such as a lead salt or an alkaline compound. Glycerol is removed continuously by stripping with a current of steam or organic solvent vapors under a reduced pressure of 40–300 mm. Analyses of a product so obtained were not given, but presumably the latter is a mixture of partial esters of the higher polyhydric alcohol. By a similar technique mannitol esters of natural oils, for use in nutritional studies, were prepared by Lapworth and Pearson[51] as long ago as 1919.

(c) Manufacture of Mono- and Diglycerides

The manufacture of commercial mono- and diglyceride mixtures represents a special case of alcoholysis wherein either fatty acids or a fat are reacted with an excess of glycerol. It is carried out on a considerable scale as a preliminary process in the preparation of alkyd resins (see page 465), to produce edible, oil-soluble surface-active agents (page 255), and for the production of detergents of the sulfonated monoglyceride type (page 394).

In the protective coating industry the reaction is usually carried out in the same kettles as are used for further reaction with resins, with the entire process being completed without cooling the initial reaction mixture or removing the alcoholysis catalyst. For edible use mono- and diglycerides are somewhat more carefully prepared in special kettles, which are preferably equipped with mechanical agitators and means for

[51] A. Lapworth and L. K. Pearson, *Biochem. J.*, *13*, 296–300 (1919).

producing a vacuum. Ordinary carbon steel is not a suitable material for the kettles, as it contaminates the product excessively with iron soap and produces a dark product; nickel, stainless steel, or aluminum are satisfactory. To the fat charge is added about 25–40% of its own weight of glycerine and 0.05–0.20% of an alkaline catalyst, such as lime, trisodium phosphate, sodium methylate or ethylate, or more usually sodium hydroxide. The catalyst reacts with the fat to form soaps, which promote the reaction at least in part, by increasing the solubility of glycerol in the fat phase.[51a] Heating of the charge is begun under reduced pressure, to remove dissolved air, and thereafter it is protected from oxidation by blanketing with an inert gas, such as nitrogen or hydrogen.
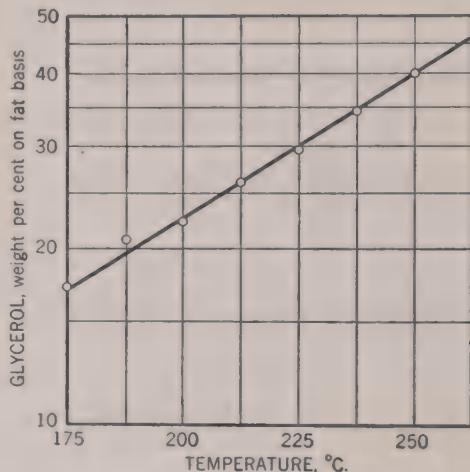
Fig. 142. Maximum amount of glycerol reactable and miscible with highly hydrogenated peanut oil in the presence of soaps from 0.1% NaOH (fat basis).[44]

drogen. The temperature is carried to a maximum of 400–475°F., usually by Dowtherm heating, and reaction is completed in 1–4 hours. At the end of this time an equilibrium will have become established between the free glycerol in the mixture and the reaction products, making it impossible for further combination of glycerol to take place.

The reaction is conducted at a high temperature partly to hasten the reaction and partly to increase the miscibility of the reaction mixture with glycerol. As Hilditch and Rigg[52] pointed out some time ago, the extent to which reaction can be carried is limited by the comparative immiscibility of glycerides and free glycerol. Any glycerol forming a second liquid phase when equilibrium is reached cannot, of course, par-

[51a] P. Savary, Compt. rend., 226, 1284–1285 (1948).
[52] T. P. Hilditch and J. G. Rigg, J. Chem. Soc., 1935, 1774–1778.

ticipate in the reaction. The maximum amount of glycerol reactable and miscible with highly hydrogenated cottonseed oil plus 0.1% sodium hydroxide (ca. 0.75% soap) has been determined at different temperatures by Feuge and Bailey[44] (Fig. 142); presumably other fats of comparable molecular weight yield similar results, although with coconut oil, etc., the solubility of glycerol is considerably greater. It will thus be seen that the proportion of glycerol that may be profitably used is dependent upon the temperature, and varies from about 22.5% of the fat at 200°C. (392°F.) to 40% at 250°C. (482°F.). Larger percentages of glycerol may be used if a large amount of soap-forming catalyst is employed,[52a] or if the reaction is conducted in a high-boiling solvent in which glycerol and glycerides are mutually soluble. Phenol or cresols were recommended as solvents by Hilditch and Rigg.[52,53] The use of dioxane has been patented by Richardson and Eckey.[54]

Batch methods for the preparation of edible mono- and diglycerides are described in a number of patents, including those issued to Edeler and Richardson[55] and Christensen.[56] Continuous manufacture has been described by Arrowsmith and Ross.[57] The reaction between fat and glycerol will take place without a catalyst being present, but the rate is reasonably rapid only at very high temperatures (500–550°F.).

There are many articles in the older literature which purport to show that temperature, the presence of catalysts, fat composition, etc., affect the composition of reaction mixtures of glycerol and fat or fatty acids. Recently, however, it has been shown[44] quite conclusively that glycerolysis, like other esterification or interesterification reactions in a homogeneous medium, proceeds substantially according to chance, producing at equilibrium a reaction mixture in which the fatty acid radicals are distributed and esterified at random among all available hydroxyl groups (see page 836). It follows, therefore, that the composition of the product, in terms of free glycerol, monoglycerides, diglycerides, and triglycerides, can be calculated from the proportions of the reactants, provided that the final mixture is homogeneous and contains no second phase of immiscible glycerol. Data for estimation of the composition of commercial mono- and diglyceride preparations, based upon cottonseed oil with an average molecular weight of 876.2, are given in Table 127. By reference

[52a] C. M. Gooding and H. W. Vahlteich (to Best Foods, Inc.), U. S. Pats. 2,197,-339–340 (1940).
[53] T. P. Hilditch and J. G. Rigg (to Imperial Chemical Industries), U. S. Pat. 2,073,797 (1937).
[54] A. S. Richardson (to Procter & Gamble Co.), U. S. Pat. 2,251,692 (1941). A. S. Richardson and E. W. Eckey (to Procter & Gamble Co.), U. S. Pat. 2,251,693 (1941).
[55] A. Edeler and A. S. Richardson (to Procter & Gamble Co.), Can. Pats. 340,803–805 (1934); U. S. Pats. 2,206,167–168 (1940).
[56] C. W. Christensen (to Armour & Co.), U. S. Pat. 2,022,493 (1935).
[57] C. J. Arrowsmith and J. Ross (to Colgate-Palmolive-Peet Co.), U. S. Pat. 2,383,-581 (1945).

TABLE 127

THEORETICAL COMPOSITION OF PRODUCTS PREPARED BY REACTION OF FAT WITH GLYCEROL.[a]

Per cent of total OH groups esterified	Parts glycerol reacted with 100 parts fat	Composition of reaction mixture, mole per cent				Composition of fatty product,[b] per cent by weight			
		Tri-	Di-	Mono-	Free glycerol	Mono-	Di-	Tri-	Glycerol content, %
100	0	100.0	0	0	0	0	0	100.0	10.51
95	0.55	85.7375	13.5375	0.7125	0.0125	0.3	9.9	89.8	11.00
90	1.17	72.9	24.3	2.7	0.1	1.2	18.7	80.1	11.53
85	1.86	61.4125	32.5125	5.7375	0.3375	2.7	26.4	70.9	12.10
80	2.63	51.2	38.4	9.6	0.8	4.7	32.9	62.4	12.71
75	3.50	42.1875	42.1875	14.0625	1.5625	7.3	38.2	54.5	13.35
70	4.50	34.3	44.1	18.9	2.7	10.5	42.5	47.0	14.03
65	5.66	27.4625	44.3625	23.8875	4.2875	14.1	45.6	40.3	14.74
60	7.01	21.6	43.2	28.8	6.4	18.3	47.7	34.0	15.48
55	8.60	16.6375	40.8375	33.4125	9.1125	22.9	48.8	28.3	16.25
50	10.51	12.5	37.5	37.5	12.5	28.0	48.8	23.2	17.06
45	12.85	9.1125	33.4125	40.8375	16.6375	33.6	47.8	18.6	17.87
40	15.77	6.4	28.8	43.2	21.6	39.6	45.9	14.5	18.71
35	19.52	4.2875	23.8875	44.3625	27.4625	46.0	43.0	11.0	19.57
30	24.52	2.7	18.9	44.1	34.3	52.7	39.3	8.0	20.45
25	31.53	1.5625	14.0625	42.1875	42.1875	59.8	34.7	5.5	21.35
20	42.04	0.8	9.6	38.4	51.2	67.3	29.2	3.5	22.27
15	59.56	0.3375	5.7375	32.5125	61.4125	75.1	23.0	1.9	23.22
10	94.59	0.1	2.7	24.3	72.9	83.0	16.1	0.9	24.16
5	199.69	0.0125	0.7125	13.5375	85.7375	91.4	8.4	0.2	25.09
0	∞	0	0	0	100.00	100.0	0	0	26.05

[a] R. O. Feuge and A. E. Bailey, Oil & Soap, 23, 259-264 (1946). Calculated on basis of random distribution in a homogeneous reaction mixture. Average molecular weight of the fat, 876.2.

[b] Composition of reaction product freed of uncombined glycerol.

to this table and Figure 142 it will be seen, for example, that at equilibrium, with a moderate amount of catalyst, the fat is miscible with about 30% of its own weight of added glycerol at 225°C. (437°F.), and that with this proportion of glycerol the glyceride portion of the reaction mixture will consist by weight of about 58% monoglycerides, 36% diglycerides, and 6% triglycerides.

In commercial preparations all of the monoglycerides consist of α-monoglycerides,[58] and these can be estimated quite easily by the periodic acid oxidation method of Pohle, Mehlenbacher, and Cook.[59] From the monoglyceride content and the total content of combined glycerol, readily determined by standard methods, calculations may be made of the percentages of mono-, di-, and triglycerides.[44,60] Commercial monoglyceride preparations usually contain about 50–60% monoglycerides and 30–45% diglycerides by analysis.[59,60] Reference to Figure 142 and Table 127 will show that higher monoglyceride contents should be obtainable by the conventional method of preparation; for example, at 250°C. (482°F.) or above it should be possible to approach 70%. At the higher temperatures, however, there appears to be a considerable tendency for monoglycerides to polymerize, yielding condensation products which are high in combined glycerol content, but which do not analyze as monoglycerides by the periodic acid oxidation method.[44] Hence, without the use of solvents or an excessive amount of catalyst, about 60% by analysis appears to be the practical maximum.

Gooding and Vahlteich[52a] have reported that by using as a catalyst sufficient sodium bicarbonate to convert about 13% of the fat to soap, they were able to produce from hydrogenated peanut oil a fat containing an average of only 1.24–1.26 fatty acid radicals per molecule of combined glycerol. This corresponds to ca. 79–82% by weight of monoglycerides. Fats of even higher monoglyceride content may be produced by fractionating commercial monoglyceride preparations by molecular distillation or solvent crystallization (see pages 388–389), and Eckey and Formo[60a] have shown that by the "directed interesterification" technique (see page 832) involving concurrent ester interchange and crystallization, a fat such as cottonseed oil can be made to precipitate its saturated fatty acids in the form of nearly pure monoglycerides or diglycerides.

Monoglyceride preparations may be washed with strong solutions of

[58] H. H. Young and H. C. Black, *J. Am. Chem. Soc., 60*, 2603–2605 (1938).
[59] W. D. Pohle, V. C. Mehlenbacher, and J. H. Cook, *Oil & Soap, 22*, 115–119 (1945). See also W. D. Pohle and V. C. Mehlenbacher, *J. Am. Oil Chem. Soc., 27*, 54–56 (1950).
[60] A. Troy and A. C. Bell, *Am. Perfumer, 48*, No. 7, 54–58 (1946).
[60a] E. W. Eckey and M. W. Formo, *J. Am. Oil Chem. Soc., 26*, 207–211 (1949). E. W. Eckey (to Procter & Gamble Co.), U. S Pat. 2,442,534 (1948).

sodium chloride, sodium sulfate, etc., for the removal of dissolved free glycerol, but the operation is difficult and not altogether satisfactory, because of the high surface activity of the material and the ease with which emulsions are formed. Frequently, free glycerol is removed by steam stripping under reduced pressure. It is necessary to conduct the stripping very carefully, however, to avoid decomposition of the product; treatment under the conditions employed in ordinary steam deodorization of edible oils will drive off most of the excess combined glycerol and cause mono- and diglycerides to revert to triglycerides. If the mono- and di-glycerides are to be incorporated into shortening, to produce a super-glycerinated product, the most satisfactory practice is to add them to the shortening while the latter is in the deodorizer, but near the end of the deodorization period, according to the method of Richardson and Eckey.[61] If the mono- and diglycerides are prepared originally from a deodorized fat, they will require very little steam stripping to constitute an accept-able ingredient of an edible fat product.

While the bulk of the glycol combined during the preparation of mono- and diglycerides is readily distilled out during deodorization, the last portions are very difficult to remove, even under the most drastic deodori-zation conditions. Decomposition of the mono- and diglycerides is facili-tated by the presence of catalysts. The experimental results in Table 128 are typical. They comprise the results of a series of tests in which hydro-genated cottonseed oil was reacted with 22% of its weight of glycerol and 0.05% of sodium hydroxide, and then steam-deodorized at 500°F. for various lengths of time, with and without decomposition of the catalyst with strong phosphoric acid. Until recently it has been accepted[58] that mono- and diglycerides were heat-labile under all conditions. Ross and co-workers[62] have shown, however, that this is not the case. In the strict absence of water or any foreign material acting as a catalyst it was found that pure monoglycerides could be heated to 200–230°C. and distilled without substantial decomposition. Similarly, these workers found that anhydrous glycerol and fat, free of soap, did not react appreciably below decomposition temperatures. The reaction between ordinary commercial materials, referred to above, is apparently catalyzed by traces of water and of the residual soap always found in alkali-refined oils.

Feuge and Bailey[44] have shown that products partially decomposed by steam deodorization do not have the same composition as normal products of equivalent combined glycerol content. As indicated graphi-cally in Figure 147 (page 837) deodorization has the effect of increasing the diglyceride content at the expense of the monoglyceride, and more

[61] A. S. Richardson and E. W. Eckey (to Procter & Gamble Co.), U. S. Pat. 2,-132,437 (1938).

[62] J. Ross, A. C. Bell, C. J. Arrowsmith, and A. I. Gebhart, Oil & Soap, 23, 257–259 (1946).

particularly, the triglyceride content of the mixture. Similar effects in deodorization are obtained with and without removal of the interesterification catalyst. In the manufacture of edible products it is important to remove the soaps formed by alkali or metal catalysts (see page 837), as these have a deleterious effect on the keeping quality of the fat.

TABLE 128
EFFECT OF STEAM DEODORIZATION AT 500°F. ON DECOMPOSITION OF MONO- AND DIGLYCERIDES

Sample	Deodorization time, hrs.	Glycerol content, %	Excess glycerol, %
Original oil..........................	—	11.25	—
Mono- and diglycerides, catalyst removed.	2	14.85	3.60
	6	13.72	2.47
Mono- and diglycerides, catalyst not removed...............................	2	11.65	0.40
	4	11.46	0.21
	7	11.30	0.05

As oil-soluble surface-active materials, mono- and diglyceride preparations are usually judged on the basis of their effectiveness in lowering
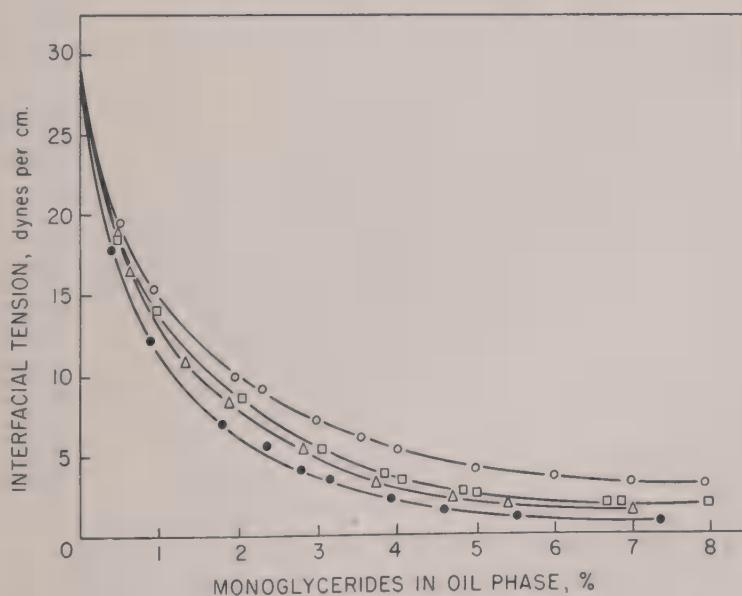
Fig. 143. Interfacial tension against water of refined cottonseed oil containing varying percentages by weight of commercial distilled monoglycerides (ca. 93–95% pure). Curves from top to bottom of diagram are for monoglycerides of mixed cottonseed oil fatty acids, triple pressed stearic acid, palmitic acid, and lauric acid.[63a]

the interfacial tension against water of fats to which they are added. A neutral oil, such as cottonseed, soybean, or peanut oil will have its

interfacial tension against water approximately halved by the addition of 1% saturated monoglycerides, and reduced to less than 1 dyne per centimeter by the addition of 6%. In commercial preparations it has been shown by Feuge[63] that lowering of the interfacial tension is caused almost wholly by the monoglycerides rather than the diglycerides present. Since common oils and fats, such as those mentioned above, have almost equal interfacial tensions (29.5–30.5 dynes per centimeter at 70°C.), and also nearly identical interfacial tensions at equivalent monoglyceride concentrations, it follows that the monoglyceride content of a product may be estimated roughly from the very simple determination of its interfacial tension by the ring method, or in terms of "drop numbers."

The data of Kuhrt and co-workers[63a] on the effect of different monoglycerides on the interfacial tension between refined cottonseed oil and water are shown in Figure 143. Additional data have been published by Feuge[63] and by Eckey and Formo[60a] (see also Figure 6, Chapter III).

3. ESTER INTERCHANGE

Ester interchange, or reaction of a fat or other mixture of fatty esters, to produce an interchange and redistribution of fatty acid radicals among the different glyceride molecules, is not of any considerable commercial importance at the present writing, but may be expected to assume importance in the future, as it constitutes a powerful tool for modification of the composition and properties of fats.

As will be explained later, ester interchange may proceed at random, with the eventual attainment of an equilibrium composition corresponding to the laws of probability; or, by special techniques, it may be directed toward some degree of segregation of the fatty acid radicals according to their degree of unsaturation or their chain lengths, with or without concurrent separation of the esters into two fractions.

(a) Applications

Because of the fact that fats or fat mixtures often have some degree of organization—produced either naturally or artificially—with respect to the distribution of their component fatty acids, profound changes in composition will often result from a random molecular rearrangement. The vegetable seed oils, e.g., cottonseed oil, peanut oil, cocoa butter, tend to have each fatty acid distributed evenly, insofar as that is possible, among the different glyceride molecules (page 5). Hence in these oils trisaturated glycerides generally do not occur in quantity unless the con-

[63] R. O. Feuge, J. Am. Oil Chem. Soc., 24, 49–52 (1947).
[63a] N. H. Kuhrt, E. A. Welch, and F. J. Kovarik, J. Am. Oil Chem. Soc., 27, 310–313 (1950).

tent of saturated fatty acids exceeds about two-thirds of the total. On the other hand, with random distribution of all acid radicals, a fat containing two-thirds saturated fatty acids will contain nearly 30% fully saturated glycerides, and even a fat containing as little as one-third saturated acids will have 3.7% fully saturated glycerides. Since the plastic range, and particularly the melting point, of a fat is highly dependent upon the trisaturated glyceride content, it follows that random re-

TABLE 129

EFFECT OF RANDOM MOLECULAR REARRANGEMENT ON MELTING POINT OF VARIOUS
FATS AND FAT MIXTURES

Fat	M.p., °F.	
	Before	After
Soybean oil[a]	19.4	41.9
Cottonseed oil[a]	50.9	93.2
Oleo stock (beef fat)[a]	121.1	120.2
Prime steam lard[a]	109.4	109.4
Palm oil[b]	103.7	116.6
Tallow (beef fat)[c]	115.2	112.3
Coconut oil[b]	78.8	82.8
Kokum butter[b]	109	146
10% highly hydrog. cottonseed oil plus 60% coconut oil[d]	136	106
25% tristearin plus 75% soybean oil[e]	140	90
50% highly hydrog. lard plus 50% lard[f]	135	123
15% highly hydrog. lard plus 85% lard[f]	124	107
25% highly hydrog. palm oil plus 75% highly hydrog. palm kernel oil[g]	122.3	104.5

[a] F. A. Norris and K. F. Mattil, *J. Am. Oil Chem. Soc.*, *24*, 274–275 (1947).
[b] E. W. Eckey (to The Procter & Gamble Co.), U. S. Pat. 2,442,531 (1948).
[c] E. W. Eckey, *Ind. Eng. Chem.*, *40*, 1183–1190 (1948).
[d] E. W. Eckey (to The Procter & Gamble Co.), U. S. Pat. 2,378,005 (1945).
[e] C. van Loon (to Naamlooze Vennootschap Anton Jurgens Margarinefabrieken), Dutch Pat. 16,703 (1927); U. S. Pat. 1,873,513 (1932).
[f] F. A. Norris and K. F. Mattil, *Oil & Soap*, *23*, 289–291 (1946).
[g] C. M. Gooding (to The Best Foods, Inc.), U. S. Pat. 2,309,949 (1943).

arrangement of a seed oil will usually change the consistency and melting point considerably, tending to raise the latter. A mixture of two radically different fats is always very far from a random distribution of fatty acids, and hence will respond to this type of interchange. In particular, it is to be noted that a mixture of a highly saturated fat with a liquid oil or an oil of the coconut type will have its melting point greatly lowered by random rearrangement (see, for example Fig. 144, page 831), through the acids of the saturated fat becoming more widely distributed.

Typical results of random rearrangement, taken from various pub-

lished articles and patents,[64-70] are shown in Table 129. As indicated above, the greatest effects are apparent when the material treated is a seed oil or a mixture of fats differing widely in melting point. Palm oil is less affected than the seed oils, insofar as melting point is concerned, and with respect to this particular characteristic animal fats such as lard or tallow are affected comparatively little. Yet more careful evaluation of these fats over a range of melting, by means of micropene-

TABLE 130

COMPARISON OF LARD PRODUCTS BEFORE AND AFTER RANDOM REARRANGEMENT: CONSISTENCY AND PERFORMANCE OF FATS IN STANDARD POUND CAKE TEST[a]

	Leaf lard		Hydrogenated lard	
Consistency and performance	Before rearrangement	After rearrangement	Before rearrangement	After rearrangement
Micropenetrations, mm./10, at:				
70°F.	62	65	40	53
80°F.	80	130	60	125
90°F.	140	225	110	285
Pound cake test (air incorporated, %):				
Period 1.	62	225	170	265
Period 2.	88	268	225	280
Period 3.	80	315	212	325
Period 4.	75	253	185	248
Loaf volume, cc./lb.	850	1495	1265	1410

[a] For a description of the pound cake test, and explanation of the mixing periods and method of calculating the per cent air incorporated in the fat, see Chapter X.

trations (see Table 130), reveals that profound changes in structure have undoubtedly taken place. From a practical standpoint, it would appear that random molecular rearrangement might be useful chiefly in treating fats or fat mixtures to destroy trisaturated glycerides and bring about distribution of the saturated fatty acids in such a manner as to produce margarine oils or confectioners' fats (hard butters) of relatively low melting point and short plastic range.[69,70]

In at least one instance, random rearrangement produces a useful result simply by breaking up the specific glycerides responsible for an undesirable crystal habit in a fat. As explained in an earlier chapter (pages 215–217), lard or hydrogenated lard has the peculiar property of form-

[64] F. A. Norris and K. F. Mattil, J. Am. Oil Chem. Soc., 24, 274–275 (1947).
[65] F. A. Norris and K. F. Mattil, Oil & Soap, 23, 289–291 (1946).
[66] E. W. Eckey, Ind. Eng. Chem., 40, 1183–1189 (1948).
[67] E. W. Eckey (to Procter & Gamble Co.), U. S. Pat. 2,378,005 (1945).
[68] E. W. Eckey (to Procter & Gamble Co.), U. S. Pat. 2,442,531 (1948).
[69] C. van Loon (to Naamlooze Vennootschap Anton Jurgens Margarinefabrieken), U. S. Pat. 1,873,513 (1932); Dutch Pat. 16,703 (1927). See also U. S. Pat. 1,744,596 (1930) and Brit. Pat. 249,916 (1924).
[70] C. M. Gooding (to Best Foods, Inc.), U. S. Pat. 2,309,949 (1943).

ing relatively large and coarse crystals, even when rapidly solidified in commercial chilling machines, and this habit is detrimental both to the consistency of the product and its performance in making certain bakery products. Rearrangement serves to make it form small crystals, with consequent improvement of the fat as a shortening agent. The beneficial effect of rearrangement on lard products is illustrated by the data in Table 130.

The process of directed rearrangement, as developed by Eckey,[66,68] is far more versatile than random rearrangement. By conducting rearrangement, and at the same time continuously removing the trisaturated glycerides that are formed from the sphere of reaction (by crystallization), it is possible to concentrate the saturated acids in a fat largely into a trisaturated glyceride fraction. Thus an effect is achieved which is in effect the reverse of random rearrangement as applied to a highly unsaturated oil mixed with a highly saturated fat. The melting point of the fat is raised, and if the fat consists of a liquid oil containing a substantial proportion of saturated acids, e.g., cottonseed or peanut oil, it is possible by this method to convert the oil into a plastic product of the consistency of shortening without resorting to the usual expedients of hydrogenating or blending with a second hard fat.[71]   The segregation of saturated acids into trisaturated glycerides is naturally accompanied by a corresponding tendency for the unsaturated acids to segregate into triunsaturated glycerides, thus breaking up the mixed saturated-unsaturated acid glycerides which are so prominent in all natural fats. As the presence of such mixed glycerides contributes to sharp melting and a short plastic range in a fat, whereas "unmixing" gives gradual melting and a long plastic range, the body characteristics of a fat are improved by directed rearrangement, even though it is originally of suitable shortening consistency.[71] The process is particularly valuable in dealing with shortenings containing considerable proportions of a natural fat of medium consistency, such as palm oil or tallow. By using larger proportions of such a fat, a low iodine value shortening agent of the puff pastry type may be produced.[72]

Obviously, directed rearrangement as described above is not suitable for the production of hard butters, which must have a low melting point and also sharp melting characteristics, or margarine fats, which must also melt completely or substantially completely at body temperature. However, it is claimed that a superior hard butter is obtained by treating coconut oil or other lauric acid oil or hydrogenated oil, with or without subsequent fractional crystallization and pressing.[73] All of the preceding

[71] E. W. Eckey (to Procter & Gamble Co.), U. S. Pat. 2,442,532 (1948).
[72] E. W. Eckey (to Procter & Gamble Co.), U. S. Pat. 2,442,537 (1948).
[73] E. W. Eckey (to Procter & Gamble Co.), U. S. Pat. 2,442,536 (1948).

directed rearrangement processes have contemplated the use of reaction and crystallization temperatures suitable for the separation of trisaturated glycerides. By operating at somewhat lower temperatures, a liquid oil may be made largely to precipitate disaturated-monounsaturated glycerides; when subsequently hydrogenated, the rearranged oil is said to yield a margarine fat with better plasticity at low temperatures than untreated oil, without the melting point or the consistency at 70–80°F. being substantially different.[74]

The directed rearrangement process is recommended[75] for the treatment of fish oils prior to fractionation of these oils to yield drying and nondrying fractions, as it facilitates the segregation of saturated fatty acids in the former fraction.

In another process,[38-40] rearrangement is directed toward a desired end by interesterifying a fat with either a monoester or an excess of free acids, and continuously distilling out the liberated acids or monoesters of low molecular weight. In this way, it is possible to impoverish either a single fat or a fat mixture of its acids of lower molecular weight, leaving the residual acids randomly distributed among the glyceride molecules. The process appears possibly to be useful for the treatment of a fat such as palm oil to improve its suitability as a shortening ingredient, and for modifying oils of the coconut oil type to make hard butters.

Owing to the fact that interesterification may be conducted at a lower temperature than is required for the direct esterification of glycerol and fatty acids, it is a useful method for preparation of the pure glycerides of acids that undergo ready polymerization. Konen and co-workers[30] have reported a case in which trielaeostearin was prepared by mixing equivalent proportions of glycerol triacetate and methyl elaeostearate with 0.05% sodium methylate, and distilling off methyl acetate at 60–100°C. under reduced pressure.

(b) Random Rearrangement

Molecular rearrangement of a triglyceride mixture occurs at an appreciable rate only at a very high temperature, when no catalyst is present. Temperatures of the order of 275–300°C. (527–542°F.) are required, and even then the reaction is slow.[67,69,76]

However, there is evidence that extensive molecular rearrangement occurs in the heat bodying of linseed oil or other drying oils at 575–600°F.[76a]

The catalysts claimed by van Loon[69] for bringing the reaction to equi-

[74] A. D. Abbott (to Procter & Gamble Co.), U. S. Pat. 2,442,538 (1948).
[75] E. W. Eckey (to Procter & Gamble Co.), U. S. Pat. 2,442,533 (1948).
[76] W. Normann, Chem. Umschau, 30, 250–251 (1923); Ger. Pat. 417,215 (1925).
[76a] L. V. Anderson and J. V. Porter, Ind. Eng. Chem., 41, 741–749 (1949).

librium within a few hours at 200–250°C. (392–482°F.) comprise the broad group of aromatic or aliphatic-aromatic sulfonic acids, metals like cadmium, lead, tin, and zinc and their compounds, and compounds of the alkali metals or of the alkaline earth metals. Examples are given of the use of metallic tin, stannous hydroxide, and sodium ethylate, and subsequent work of other investigators indicates that these, and closely related catalysts, are in fact the most effective. In a series of comparative experiments with equal percentages by weight of different catalysts, Desnuelle and Naudet[77] found that sodium methylate, sodium ethylate, tin, and zinc were comparatively effective and of decreasing activity in the order named, whereas sodium carbonate, benzene sulfonic acid, and p-toluene sulfonic acid were somewhat less effective. Norris and Mattil[65] were unable to obtain any appreciable reaction with the use of sodium hydroxide.
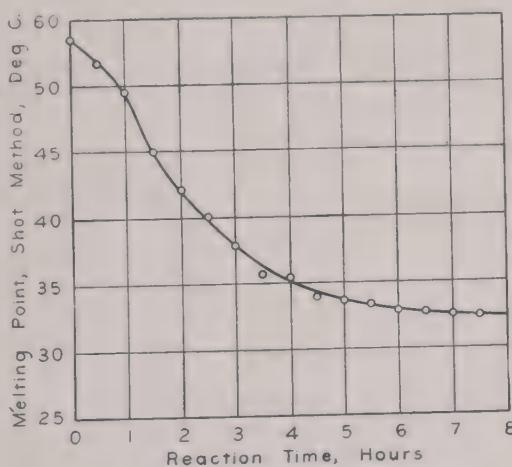
Fig. 144. Change of melting point with reaction time in a mixture of 15% cottonseed oil stearine and 85% soybean oil subjected to rearrangement at 450°F. with stannous hydroxide equivalent to 0.39% tin as a catalyst.

The experience of the author has been that a stannous hydroxide catalyst is superior to other heavy metal catalysts, but that the preparation and use of the catalyst is somewhat critical. An active catalyst may be prepared by the following procedure:

45 parts by weight of stannous chloride ($SnCl_2 \cdot 2H_2O$) are dissolved in 3000 parts of water, in which is suspended 40 parts of diatomaceous earth. To this is added slowly with stirring 500 parts of water in which have been dissolved 25 grams of sodium carbonate (Na_2CO_3). The precipitate is filtered and washed with cold water. The fresh wet filter cake is added directly to the reaction vessel. Cadmium and lead catalysts prepared by a

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[77] P. Desnuelle and M. Naudet, *Bull. soc. chim.*, **13**, 90–94 (1946).

similar procedure are also active. The stannous hydroxide catalyst loses much of its activity if it is dried, or even stored for a long time in the wet form, and is also almost inactive if filtered out of the reaction mixture and re-used.

In Figure 144 are shown graphically the results of a test in which there was reacted at 450°F. under an atmosphere of hydrogen a fat containing an amount of the above catalyst equivalent to 0.39% tin. The fat in this case was a mixture of 15% highly hydrogenated cottonseed oil with soybean oil, the extent of rearrangement being indicated by the decrease in the melting point of the mixture.

Fats respond more readily to rearrangement with the above catalysts if they are substantially devoid of free fatty acids. As reaction proceeds, there always appears to be some degree of splitting to produce unesterified hydroxyl groups, and there is reason to believe that the presence of free hydroxyl groups is, in fact, essential for the continued interchange of fatty acid radicals. Gooding[70] has shown that a random molecular rearrangement occurs rapidly if the reaction is carried out in the presence of a slight excess of glycerol or other high-boiling alcohol. In this case, rearrangement is greatly assisted by the presence of a small amount of sodium hydroxide or other material capable of catalyzing the formation of mono- and diglycerides. In practice, relatively large amounts of glycerol, e.g., 2 to 5%, and a very high temperature, 500° to 525°F., are required to complete the rearrangement in 6 hours or less, in the absence of an alkaline assisting catalyst. If 0.05% of sodium hydroxide is used, the glycerol may be reduced to as little as 0.2 to 0.5% and the temperature may be as low as 450°F. In the process patented by Eckey[67] free hydroxyl groups are maintained by conducting the reaction under pressure in the presence of water to hydrolyze the fat partially. An example is cited in which fat was reacted with 10% of its own weight of water at 235–240°C. for one hour. After removal of the water, the reaction mixture was further heated for one-half hour at 260°C. to effect re-esterification of free hydroxyl groups with the free acid.

As an alternative to the use of a free alcohol as such, rearrangement may of course be carried out by adding preformed mono- and diglycerides. Virtually the same result is obtained by the method patented by Grün,[37] which comprises forming mono- and diglycerides by heating the fat with a catayst such as metallic tin, and thereafter converting the former to triglycerides by further reaction with free acids.

(c) Directed Rearrangement

The directed rearrangement process of Eckey,[66,68] referred to earlier, is based upon the discovery that, under special conditions, ester inter-

change can be carried out at such a low temperature that simultaneous crystallization of glycerides will affect the result.

As a catalyst, sodium methylate (sodium methoxide) is ordinarily used, because of its low cost, stability, and ease of preparation, although other alcoholates of sodium or potassium are also effective. Since addition of the catalyst to the fat is followed at once by the appearance of an equivalent amount of fatty acid methyl ester, it is believed that the compound actually performing the catalytic role is not the alcoholate, but a reaction product of the latter with the glycerides, or in other words a fat–sodium compound of unknown constitution. Alternative ways of forming this compound are known, including the addition to a fat of metallic potassium in xylene, anhydrous potassium hydroxide in undecane, or an organic sodium or potassium compound with the alkali metal bound directly to a carbon atom, as in triphenylmethyl sodium. It is essential that no water be present, to form soap, that the fat be acid-free and peroxide-free, and that the catalyst be rapidly dispersed through the reaction mixture immediately after it is added. In practice, it is convenient to form the sodium methylate by reacting molten sodium with anhydrous methanol in a dry solvent such as xylene, handling it thereafter as a suspension in xylene.

The preferred concentration of catalyst (sodium methylate) is 0.05–0.20%; with this concentration the reaction is usually substantially complete within 24 hours, at 80–100°F., although somewhat longer may be required at lower temperatures. Since all fats supercool greatly, the attainment of equilibrium may be hastened by "seeding" the fat with crystals before the catalyst is added. Seeding of the fat is said to be particularly desirable if it is desired to conduct the reaction at a relatively low temperature, to permit separation of a large proportion of mixed disaturated monounsaturated glycerides.[78] If fractional crystallization of the rearranged fat is also contemplated, the reaction may be conducted in an inert solvent, such as a hydrocarbon fraction. Somewhat surprisingly, the reaction is said to continue to progress, without the aid of stirring or agitation, in a fat which has become too firm to be worked in any way. After a fat is treated, the catalyst must of course be inactivated before the fat can be melted (or even heated), to avoid disturbance of the equilibrium attained. This is carried out by mixing or macerating the fat with an acidic material, e.g., dilute phosphoric or glacial acetic acid.

[78] E. W. Eckey (to Procter & Gamble Co.), U. S. Pat. 2,442,535 (1948).

E. Composition of Glycerides with Randomly Distributed Fatty Acid Radicals

Formulas for calculating in terms of glycerides the composition of a re-esterified or randomly rearranged fat are easily derived from probability considerations, and are as follows:

Where A, B, C, D, etc. are the molar percentages of fatty acids a, b, c, d, etc. in the fat, the molar percentage of a glyceride containing only one of the fatty acids will be the cube of the molar percentage of the fatty acid, divided by 10,000. For example:

$$\text{Per cent glyceride } a\text{-}a\text{-}a = (A.A.A)\ 1/10,000$$

The molar percentage of a glyceride containing two different fatty acids will be the square of the molar percentage of the fatty acid occurring twice, times the molar percentage of the fatty acid occurring once, times 3, divided by 10,000. For example:

$$\text{Per cent glyceride } a\text{-}a\text{-}b = (A.A.B)\ 3/10,000$$

The molar percentage of a glyceride containing three different fatty acids will be the product of the molar percentages of the three acids, times 6, divided by 10,000. For example:

$$\text{Per cent glyceride } a\text{-}b\text{-}c = (A.B.C)\ 6/10,000$$

The use of the above formulas will be illustrated by a single example. Suppose that re-esterified or randomly rearranged fat contains stearic, oleic, and linoleic acids in the following molar proportions:

Stearic acid	20%
Oleic acid	30%
Linoleic acid	50%
Total	100%

The molar proportions of the various glycerides will be as follows:

Stearic-stearic-stearic	$= (20.20.20)\ 1/10,000 =$	0.8%
Oleic-oleic-oleic	$= (30.30.30)\ 1/10,000 =$	2.7
Linoleic-linoleic-linoleic	$= (50.50.50)\ 1/10,000 =$	12.5
Stearic-stearic-oleic	$= (20.20.30)\ 3/10,000 =$	3.6
Stearic-stearic-linoleic	$= (20.20.50)\ 3/10,000 =$	6.0
Oleic-oleic-stearic	$= (30.30.20)\ 3/10,000 =$	5.4
Oleic-oleic-linoleic	$= (30.30.50)\ 3/10,000 =$	13.5
Linoleic-linoleic-stearic	$= (50.50.20)\ 3/10,000 =$	15.0
Linoleic-linoleic-oleic	$= (50.50.30)\ 3/10,000 =$	22.5
Stearic-oleic-linoleic	$= (20.30.50)\ 6/10,000 =$	18.0

$$Total = 100.0\%$$

The calculation of the percentages of mono-, di-, and triglycerides and

of free glycerol or other free alcohol in an alcoholized fat at equilibrium is very similar. Here, it is necessary first to determine from the proportions of the reactants the molar percentages of the total hydroxyl groups that are esterified and unesterified. Then, designating the esterified per-
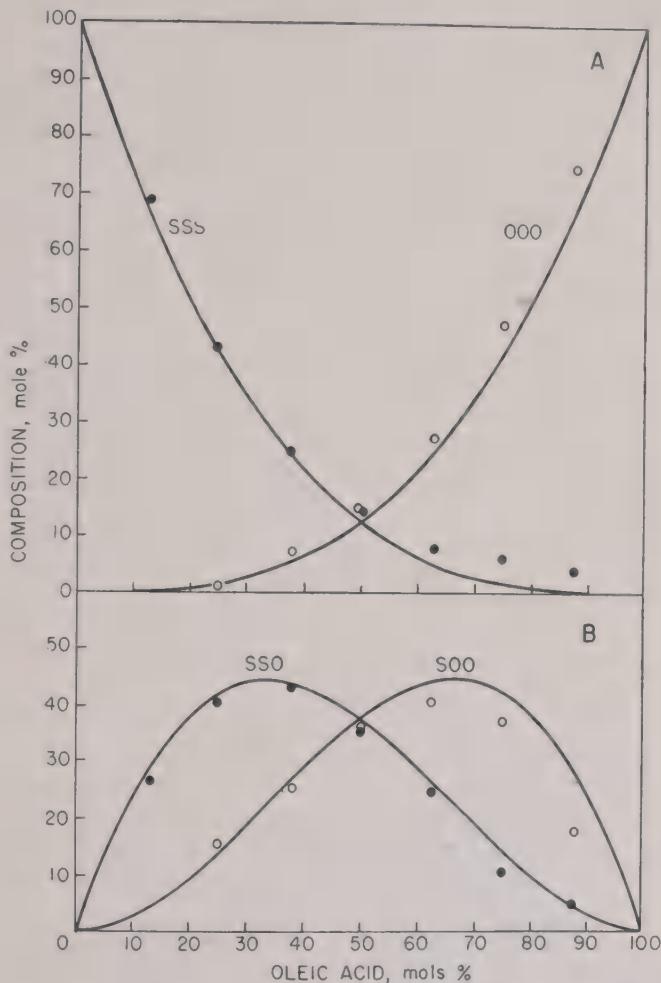
Fig. 145. Composition of interesterified triglycerides containing stearic and oleic acids in different proportions. (Curves represent compostion calculated on basis of random distribution; plotted points represent experimentally determined composition.)[79]

centage as A and the unesterified percentage as B, calculations may be made of a-a-a or triglycerides, a-b-b or diglycerides, a-a-b or monoglycerides, and b-b-b or free alcohol, utilizing the formulas given above for rearranged fats. Again an example may be given. If one mol of a neutral fat is reacted with nine mols of glycerol, 25% of the total hydroxyl groups will be esterified and 75% must be unesterified. At equi-

librium, then, the molar percentages of the different components will be
as follows:

Per cent triglyceride $(a$-a-$a)$ = $(25.25.25)$ $1/10,000$ = 1.5625%
Per cent diglycerides $(a$-a-$b)$ = $(25.25.75)$ $3/10,000$ = 14.0625%
Per cent monoglycerides $(a$-b-$b)$ = $(25.75.75)$ $3/10,000$ = 42.1875%
Per cent free glycerol $(b$-b-$b)$ = $(75.75.75)$ $1/10,000$ = 42.1875%

For a tabulation of calculated compositions with other proportions of
reactants, reference may be made to Table 127.
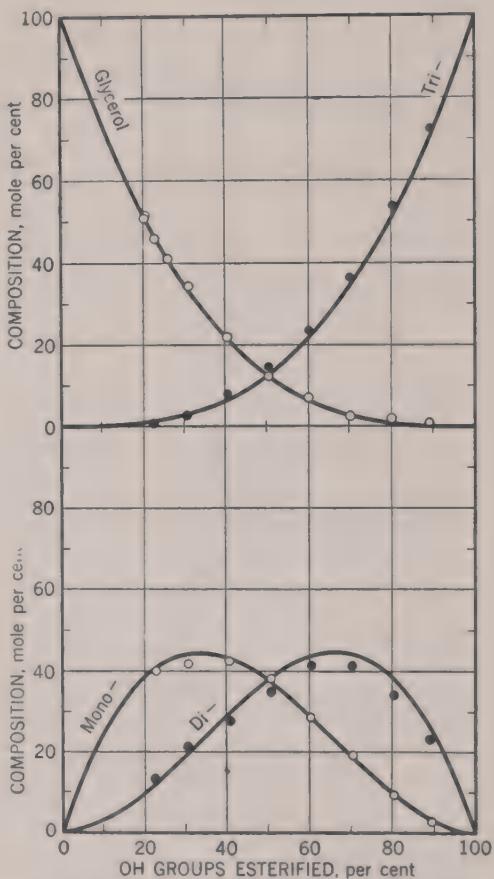
Fig. 146. Composition at equilibrium of single-phase reaction mixtures of highly
hydrogenated peanut oil with an excess of glycerol. (Curves represent composition
calculated on the basis of random distribution; plotted points represent experi-
mentally determined compositions.)[44]

That a re-esterified fat has a random distribution of fatty acids inso-
far as its trisaturated glyceride content is concerned was discovered by
Bhattacharya and Hilditch,[18] and Norris and Mattil[65] have established
that the same applies to fats interesterified by the method of van Loon,
with a wet stannous hydroxide catalyst. More recently, Naudet and

Desnuelle have developed a technique[77] for the estimation of trisaturated, disaturated, monosaturated, and triunsaturated glycerides in mixtures containing combined stearic and oleic acids, and have applied it[79] to the analysis of tristearin and triolein interesterified in different proportions with a sodium methylate catalyst at 205°C. Their results, shown graphically in Figure 145, conform unmistakably to the random distribution pattern, even though certain irregularities are apparent, probably from the lack of precision of the analytical method, and possibly a failure in some cases to carry the reaction to equilibrium.

Feuge and Bailey[44] have alcoholized a highly hydrogenated cottonseed oil with various proportions of glycerol under conditions chosen to pro-
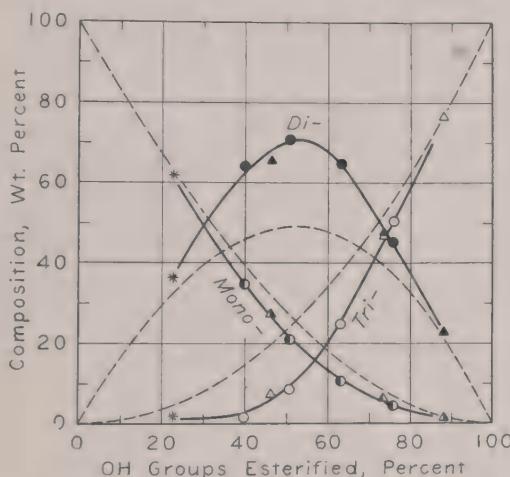
Fig. 147. Composition of a mono- and diglyceride preparation after partial decomposition by steam deodorization. (Solid curves and plotted points represent compositions determined experimentally after deodorization at different temperatures, with and without destruction of the catalyst; broken curves represent compositions corresponding to random distribution.)[44]

duce a homogeneous reaction mixture, and have analyzed the equilibrium mixture for triglycerides, diglycerides, monoglycerides, and free glycerol. The results, shown in Figure 146, amply confirm the random distribution hypothesis. As indicated previously (page 824), the random distribution pattern is destroyed if the mono- and diglycerides are partially decomposed by steam deodorization. The deviation from random distribution in steam-deodorized material is shown graphically in Figure 147.

F. Removal of Esterification Catalysts

Nonedible oils and fats, and particularly those destined for use as drying oils, often do not require removal of the esterification catalyst. On

[79] M. Naudet and P. Desnuelle, *Bull. soc. chim.*, *14*, 323–325 (1947).

the other hand, it is almost invariably necessary to free edible fats of any residue of heavy metals or metal soaps, because of the toxicity of these, and of any alkali or alkali metal soaps, because of their detrimental effect on the stability of the fats.

Neutral fats or fats containing an excess of fatty acids and no partial esters are most conveniently purified by ordinary alkali refining, followed by treatment with bleaching earth. Feuge *et al.*[20] have investigated the removal of tin and zinc from re-esterified fats to which these metals had been added as catalysts in the form of their chlorides. The tin content of the fat was reduced below the limit of spectrochemical analysis, *i.e.*, below 0.00032%, by refining with caustic soda solution in 0.40% excess. By similar refining the zinc content was reduced to 0.0001%, and further treatment with 4% of natural bleaching clay reduced the zinc below the limit of detection (0.00001%). Washing with 20% sulfuric acid solution reduced the zinc content to 0.0001%, but left nearly one-tenth (0.0113%) of the tin in the fat.

Commercial mono- and diglyceride preparations or other alcoholized products cannot, of course, be alkali-refined, and, in fact, washing or any other treatment with aqueous media is very difficult, because of the surface activity of the partial esters and their tendency to form stable emulsions. Eckey and Clark[80] have devised a novel method of destroying the catalyst without washing. The batch is cooled to about 190° to 210°F., and sufficient 85% phosphoric acid is added to decompose the soaps and provide about 50% excess, along with a small quantity of diatomaceous earth or other filter aid. The mixture is then stirred under a vacuum for a few minutes, and filtered. Dehydration of the mixture occurs, and the soaps are decomposed to form free fatty acids and sodium phosphate. The sodium phosphate is insoluble in the oil, and hence is removed with the filter aid. In the above-cited experiments of Feuge *et al.*[20] treatment with phosphoric acid according to this procedure was effective in removing tin (to below 0.00032%) but not in removing zinc, which persisted to the amount of 0.0094% in a fat originally containing 0.036%.

Brown, Grettie, and Phelps[81] have patented more or less similar methods for destroying alkaline catalysts with acids such as citric, maleic, oxalic, tartaric, or sulfuric. All of these acids, and also phosphoric acid, it may be noted, are synergists for the antioxidant effect of the tocopherols present in natural oils, and hence their use may be expected to improve rather than impair the stability of the fats.

[80] E. W. Eckey and C. C. Clark (to Procter & Gamble Co.), U. S. Pat. 2,065,520 (1936).
[81] L. C. Brown, D. P. Grettie, and G. W. Phelps, Can. Pats. 389,953–957 (1940).

Treatment of monoglycerides, etc., with an acid to decompose soaps and precipitate a salt, will, of course, leave a corresponding amount of free fatty acids in the material. This may be undesirable, particularly if a large amount of catalyst is used. To avoid the production of free fatty acids, Gooding and Vahlteich[52a] recommend treating the reaction mixture with a mineral acid ester of the alcohol, *e.g.*, glycerol chlorohydrin or the reaction product of glycerol and sulfuric acid.

SOAPMAKING[1]

A. Introduction

1. Nature of the Soapmaking Process

The basic reaction in soapmaking is, from a purely chemical standpoint, quite simple. It consists of reacting fat with an alkali to produce soap and glycerol:

$$C_3H_5(OOC.R)_3 + 3\,NaOH = 3\,Na.OOC.R + 3\,C_3H_5OH$$

Triglyceride   Caustic soda   Sodium soap   Glycerol
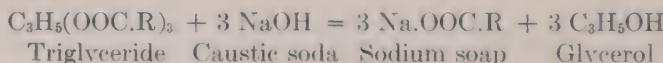
That the technology of soapmaking is involved, and that practical soapmaking borders at times on an art, is due to the extraordinarily complex physical nature of soap and its aqueous systems. Subsequent to saponification, which is in itself an exacting operation, the soap must be carried through a series of phase changes for the removal of impurities, the recovery of glycerine, and reduction of the moisture content to a relatively low level.

The complete series of operations in the production of an ordinary full-boiled or settled soap is as follows: (a) reaction of the fat with alkali until it is largely saponified; (b) graining out of the soap from solution with salt in two or more stages, for recovery of the glycerol produced by the reaction; (c) boiling of the material with an excess of alkali to complete saponification, followed by graining out with alkali; and (d) separation of the batch into immiscible phases of neat soap and niger— the so-called "fitting" operation.

The "neat soap," consisting of about 65% real soap with about 35% water, and with traces of glycerine, salt, etc., is the product from which —with or without drying, mechanical working, and addition of nonsoap ingredients—are formed most commercial bars, flakes, granules, and powders.

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[1] For details of the practical aspects of soapmaking, see E. T. Webb, *Modern Soap and Glycerine Manufacture*, Davis Bros., London, 1927; G. Martin, *The Modern Soap and Detergent Industry*, 2nd ed., Lockwood, London, 1931; H. Schönfeld, ed., *Chemie und Technologie der Fette und Fettprodukte*, Vol. IV, Springer, Vienna, 1939; J. H. Wigner, *Soap Manufacture*, Chemical Pub. Co., Brooklyn, 1940; A. Kufferath, *Die Seifenherstellung*, Hartleben, Vienna, 1942; E. G. Thomssen and J. W. McCutcheon, *Soaps and Detergents*, MacNair-Dorland, New York, 1949.

The following sections describe the operation of soap boiling in a general way, and are of course not intended to constitute a manual for the operation of this difficult process.

2. Historical

Soapmaking has undoubtedly been practiced for well over 2000 years. The origins of the process are lost in prehistory, but it is known that the ancient Romans made and used considerable quantities of soap before the Christian era; a complete factory for soapmaking was preserved in the city of Pompeii, which was buried in 79 A.D.

During the Middle Ages the art survived in certain cities in Italy, France, and England. In the 18th century it had reached a high state of development in a number of places, notably in Marseilles, which is still an important center. Early soapmakers followed the laborious practice of leaching potassium carbonate from wood ashes, causticizing this with slaked lime and using the caustic potash for saponification. For production of hard soaps it was necessary to salt out the resultant soft potash with common salt.

In the 19th century, following the introduction of the LeBlanc process for caustic soda manufacture, soap became much cheaper, and its use became very common.

B. Soap Boiling

1. Equipment for Soap Boiling

The boiling of soap is carried out in large cylindrical kettles with cone bottoms, equipped with open and sometimes with closed coils for steam (in Europe square kettles or "pans" are often used). They are provided with delivery pipes for fat, water, lye, brine, and niger or other soapstocks brought from other parts of the plant. A swinging suction or "skimmer" pipe operated from the top is installed to permit drawing off the contents to any desired level, and in the bottom another line is provided for withdrawing the residue left from skimming. Since contamination of the soap with rust is very undesirable, the steel kettles are now commonly clad with nickel or other corrosion-resistant metal, at least down to below the usual liquid level.

Soap kettles are preferably made as large as the production of the plant will reasonably permit; in the larger plants they often have a total water capacity of several hundred thousand pounds, and seldom, except in the smallest plants, is this capacity less than about 150,000 pounds. In order that the soap batch may not cool and become excessively viscous during a prolonged period of settling neat soap from niger, the kettles

must not be too small. Further, a large batch requires no more of a soap boiler's expert attention than a small one. A typical kettle will have a capacity of about 8000 cubic feet, and a water capacity of 500,000 pounds. The batch is often started on the niger from a previous boil; the fat charge must not exceed about 25–30% of the water capacity of the kettle, and hence a kettle of this size will take about 125,000 pounds of fat, plus 50,000 pounds of niger. From this the yield will be about 200,000 pounds of neat soap, plus 50,000 pounds of niger to be used in starting another batch.

2. SELECTION OF FAT CHARGE

Since the choice of fatty materials for soapmaking has been discussed in a previous chapter, it will only be repeated here that the principal considerations are the provision of a fat mixture containing saturated and unsaturated, and long and short chain fatty acids in suitable proportions to yield the desired qualities of stability, hardness, solubility, ease of lathering, etc., in the finished product, and sufficient refining and bleaching of the fat charge to insure a good appearance. A very common mixture for the manufacture of toilet soaps is about 75% tallow and 25% coconut oil. To produce a white toilet soap of sufficiently light color Thomssen and McCutcheon[2] recommend that the color of the tallow be not darker than 3 on the F.A.C. scale, and that the coconut oil have a Lovibond color not in excess of 10 yellow and 2 red.

As a general rule for the selection of a fat charge the empirical I.N.S. method of Webb[2a] deserves some mention. The I.N.S. factor of a fat is defined as the saponification value minus the iodine value; the I.N.S. factor of a mixture of fats is calculated proportionally from the factors of the individual fats. In a mixture, the S.R. factor is calculated by dividing the I.N.S. factor as defined above by another similar factor in which the individual I.N.S. factors of coconut and palm kernel oil and all liquid oils (with I.N.S. less than 130) are taken as zero. For toilet soaps an I.N.S. factor of 160–170 and an S.R. factor of 1.3–1.5 are recommended.

Blending of different materials to produce soap with the desired characteristics is invariably carried out with the fats before they are saponified. Except to a limited degree in certain special products it is not practicable to blend different stocks after they are saponified, although the so-called soap builders and other nonsoap ingredients are mixed in after saponification is completed.

[2] E. G. Thomssen and J. W. McCutcheon, *Soaps and Detergents*. MacNair-Dorland, New York, 1949.
[2a] E. T. Webb, *Modern Soap and Glycerine Manufacture*. Davis Bros., London, 1927.

3. PHYSICAL CHEMISTRY OF THE SOAP KETTLE

The physicochemical nature of soaps and soap solutions has been discussed at some length in a previous chapter (pages 344–365), hence it is necessary here to consider only the system of soap, water, and electrolyte existing at approximately 100°C. in the soap kettle. Such a system is represented in part in the diagram of Figure 148. In the present discussion this diagram is intended to be illustrative only, although the phase boundaries have been placed reasonably close to those actually reported by different workers[3] for representative commercial soaps. The various operations in soap boiling are best explained with reference to this diagram.

As explained in a previous chapter (Chap. XI), the use of phase diagrams for commercial soaps is fully justified, as the work of McBain, Ferguson, and others has shown that these soaps behave essentially like salts of single fatty acids, with negligible fractionation of the individual components occurring upon separation of the soap into two phases or partial transformation of the soap from one phase to another.

In the diagram the per cent by weight of anhydrous soap is plotted along the vertical axis, and the per cent by weight of salt (sodium chloride) is plotted along the horizontal axis. The weight per cent of water is, of course, 100% minus the combined percentages of water and salt; hence the composition of any combination of soap, water, and salt can be represented by a single point. While but one electrolyte, sodium chloride, has been represented, the effect of mixed electrolytes in such systems is additive[4]; hence the diagram may also be considered to indicate the action of caustic soda or mixtures of caustic soda and salt, calculated in terms of sodium chloride. The glycerol present in the system may be disregarded, as it has been shown[5] that it behaves toward the soap similarly to water. Certain boundaries in the upper portion of the system have been omitted. However, this portion is but poorly explored, and, in any case, it is not important in the present discussion.

In Figure 148 are to be seen four one-phase regions A, B, D, and J, comprising, respectively, neat soap, middle soap, niger (isotropic solution), and kettle wax (usually referred to by the practical soap boiler as "curd"). The horizontal ordinate constitutes, of course, an additional

[3] R. H. Ferguson, *Oil & Soap*, *9*, 5–8 (1932). R. H. Ferguson and A. S. Richardson, *Ind. Eng. Chem.*, *24*, 1329–1336 (1932). J. W. McBain, W. J. Elford, and R. D. Vold, *J. Soc. Chem. Ind.*, *59*, 243–252 (1940). J. W. McBain, R. D. Vold, and K. Gardiner, *Oil & Soap*, *20*, 221–223 (1943). J. W. McBain, K. Gardiner, and R. D. Vold, *Ind. Eng. Chem.*, *36*, 808–810 (1944).
[4] J. W. McBain and A. V. Pitter, *J. Chem. Soc.*, *1926*, 893–898.
[5] R. H. Ferguson, *Oil & Soap*, *14*, 115–118 (1937).

single-phase region consisting of "lye" or soap-free electrolyte, but existing here in one dimension only.

There are six two-phase regions, represented by C, E, F, I, K, and M. In the figure these have a shaded appearance, from the tie lines which have been drawn in. It is important to remember that when the composition of the system is brought into one of these regions the *composition* of each phase separating will be represented by the ends of the tie line passing through that particular composition. Also, the *amounts* of each phase produced can be calculated from lengths measured on the tie line according to the so-called "lever principle." Thus, for example, if the system is brought to the composition represented by y, so that separation
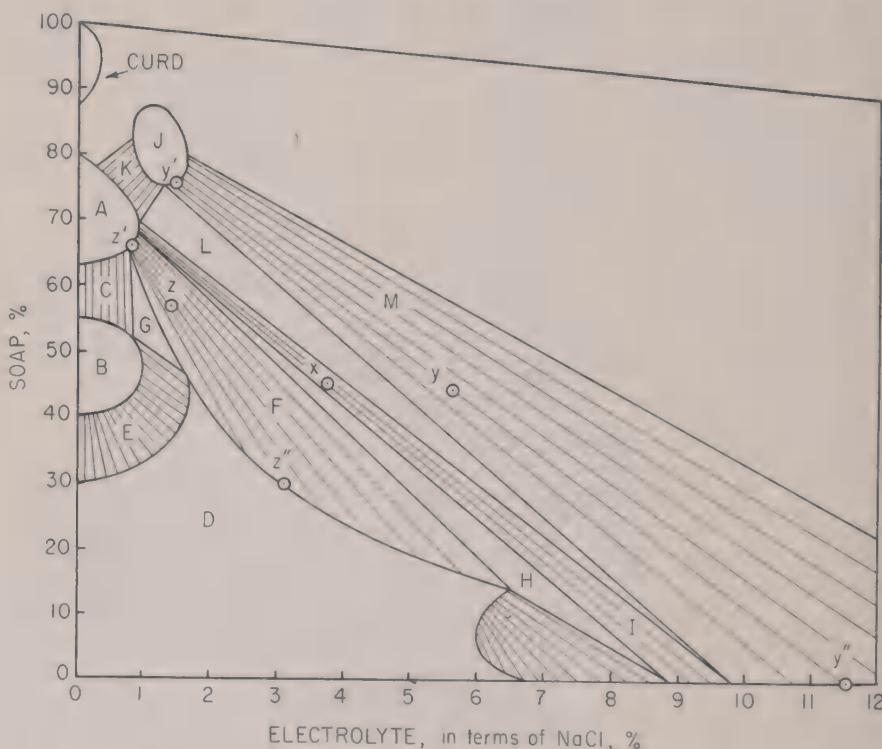
Fig. 148. Illustrative phase diagram showing phase relationships in soap boiling; for explanation, see text.

occurs into kettle wax and lye, the composition of these two phases will be represented by y' and y'', respectively. The fraction of kettle wax will then be equal to $yy''/y'y''$, and the fraction of lye will be equal to $yy'/y'y''$.

Finally, there are three triangular three-phase regions: G, H, and L. In each of these the composition of the three phases separating is the same *throughout the region*, and is represented by the apexes of the triangle.

4. THE SAPONIFICATION REACTION

The successive operations performed on a single batch of material in the soap kettle to produce a "settled" soap are termed "changes." The first of these, which is designed to effect saponification of the greater part of the fresh fat, is often referred to as the "killing change." It is carried out by boiling the fat and alkali together with open steam. Since neutral fat and aqueous alkali solution are immiscible, the reaction rate is at first slow, and principally dependent upon the magnitude of the interface between the two liquids. In the later stages, however, saponification may be considered an essentially homogeneous reaction, proceeding through concurrent solution of fat and alkali in a phase consisting of preformed soap. The reaction, therefore, is markedly autocatalytic. If the amount of fat saponified is plotted against reaction time, a sigmoid curve results; the reaction, at first slow, accelerates rapidly as increased quantities of soap are formed, and slows again only toward the end, as the concentration of fat becomes low, and considerable proportions of fat tend to become occluded among alkali-improverished soap micelles. The marked ability of strong soap solutions to dissolve neutral fats and the significance of this phenomenon in soapmaking was perhaps first pointed out by Smith,[6] and is now generally recognized.[7]

In technical practice, soap is often boiled on a niger of preformed soap left from a previous boil. Fresh fat and alkali slowly added to the boiling soap mass saponifies very rapidly. However, considerable heat (about 65 cal. per kilogram of fat saponified) is evolved in the reaction, and the addition of fat and lye must be carefully controlled to avoid boiling the batch out of the kettle from the excessively rapid generation of heat.

Although saponification may occur in successive stages:

$$
\begin{array}{ccc}
\text{H} & & \text{H} \\
| & & | \\
\text{H—C—OOC.R}_1 & & \text{H—C—OH} \\
| & & | \\
\text{H—C—OOC.R}_2 + \text{NaOH} & = & \text{H—C—OOC.R}_2 + \text{Na.OOC.R}_1, \text{ etc.,} \\
| & & | \\
\text{H—C—OOC.R}_3 & & \text{H—C—OOC.R}_2 \\
| & & | \\
\text{H} & & \text{H}
\end{array}
$$
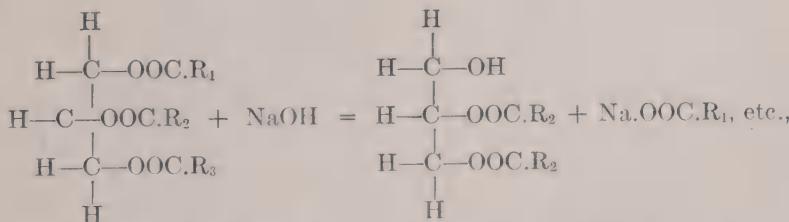
it has been shown by Kellner[8] that there is no accumulation of mono- or diglycerides in the reaction mass at any stage of the process. Since free fatty acids react more readily with alkali than do glycerides, a fat charge containing some proportion of free fatty acids is saponified more readily than one which is substantially neutral. Fats of a relatively low degree of unsaturation saponify more readily than more highly unsaturated fats,

[6] E. L. Smith, *J. Phys. Chem.*, *36*, 1401–1418 (1932).
[7] See, for example, L. Lascaray, *Fette u. Seifen*, *46*, 531–536 (1939).
[8] J. Kellner, *Chem.-Ztg.*, *33*, 453 (1909).

but there appears to be no relationship between saponification rate and molecular weight of the acids.[9]

That coconut oil saponifies somewhat more readily than equally saturated fats of higher molecular weight is believed[9a] to be due to the greater surface activity of soaps of the C_{12} and C_{14} acids formed during the early part of the reaction, rather than to greater reactivity of the lower acids.

The fresh lye used for the killing change commonly has a strength of about 30° Bé., corresponding to a sodium hydroxide content of 23.5%. The amount of such lye required for complete saponification is for most stocks in the range 60–65 pounds per 100 pounds of fat. However, the use of so-called "half-spent" lyes, the condensation of steam, and the practice of boiling upon a previous niger increase the minimum weight ratio of soap to lye, and at the end of the saponification step the soap content of the kettle is usually in the neighborhood of 50%.

During the boiling operation it is necessary to keep the composition of the batch reasonably well within the portion of the diagram comprising areas F, H, and I (Fig. 148). This can be done only by maintaining an excess of alkali during the first part of the operation, and adding salt or strong brine, to increase the electrolyte concentration, as the alkali decreases toward the end of the reaction. If the composition is allowed to come within areas B, C, E, or G, thickening or "bunching" will occur, from the formation of middle soap. This phase appears in the form of very viscous, gummy lumps, which are difficult to eliminate once they are produced in quantity. It is to be noted that middle soap may be formed locally if the batch is not boiled vigorously and poor mixing occurs, even if the total composition of the batch is correct. On the other hand, if the composition is allowed to enter areas L or M, through alkali being present in too great excess, "curd" soap will separate and this will retard saponification, as this soap is a poorer reaction medium than neat soap. Neat is also a better medium for reaction than is niger; hence it is desirable to keep the batch just barely "closed" or liquid, at a composition, for example, as represented at x in Figure 148. The condition of the batch throughout the operation is judged by the soap boiler almost entirely according to its appearance in the kettle, or as withdrawn in small portions on a trowel, and according to the degree to which excess alkalinity produces a "bite" on the tongue. However, phenolphthalein or other indicator may be used as an auxiliary guide to the progress of the reaction.

Since the lye, or soap-free liquor produced by the killing change is

[9] J. W. McBain, C. W. Humphreys, and Y. Kawakami, *J. Chem. Soc.*, *1929*, 2185–2197.
[9a] C. Bergell and L. Lascaray, *Siefensieder Ztg.*, *52*, 191–194 (1925).

processed directly for glycerine recovery, it is customary to finish this change with a virtually neutral lye and an excess of unsaponified fat (usually about 2–10% of the original amount) remaining. Saponification of the fat is completed in a subsequent operation.

Roshdestvenskii[10] found that the saponification rate is greatly increased by the presence of ca. 1% of certain phenols, cresols, etc., e.g., β-naphthol. These saponification catalysts are particularly effective for oils of relatively high unsaturation. They have been used to some extent by European soapmakers, but apparently have been little used in the United States.

5. Graining Out and Washing

Following saponification, the soap is grained out by the addition of salt to the boiling mass. Practice varies in the use of salt; some operators use dry salt, which is sprinkled over the surface of the kettle, while others prefer to use a strong brine. If brine is used, more water must be evaporated in the subsequent recovery of glycerine, but, on the other hand, it is more easily handled than dry salt.

The object of graining out is to bring the system into region M (referring again to Fig. 148), so that the soap may be separated from the "spent" glycerine-containing lye. The soap rises to the top of the kettle in the form of rough masses commonly referred to as "curd." McBain and co-workers[11] have shown, however, that this soap is not identical with the crystalline curd which is produced by cooling neat soap, and which exists at 100°C. at a higher soap concentration, but is a form which they have designated as "kettle wax." This form, of waxy texture at soap-boiling temperatures, is converted to a white solid curd upon cooling. The point y in Figure 148 represents the total composition of a representative batch brought to the point of graining out, with points y' and y'' representing the composition of "curd" and lye, respectively.[12]

The greater part of the glycerine is recovered in the liquor drawn off from the first or killing change; in noncountercurrent operation, the spent lye may contain up to 6–8% glycerine. However, it is necessary to carry out further brine changes or "washes" to make recovery substantially complete. These are carried out by adding water to the curd mass again to bring the composition of the batch into the closed or liquid

[10] D. Roshdestvenskii, *Seifensieder-Ztg.*, **55**, 127–128, 166–167 (1928).
[11] J. W. McBain, R. C. Thorburn, and C. G. McGee, *Oil & Soap*, **21**, 227–230 (1944). J. W. McBain, K. Gardiner, and R. D. Vold, *Ind. Eng. Chem.*, **36**, 808–810 (1944).
[12] Actually, due to mechanical inclusion of lye in the "curd," the latter will have a total composition somewhat different from that indicated, after the lye is drawn off. Ordinarily the anhydrous soap content of the curd mass is about 60–64%.
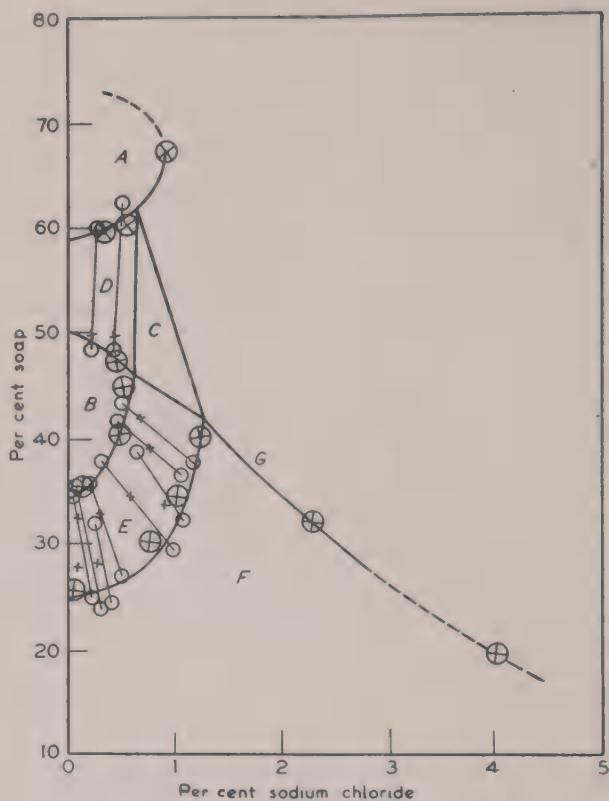
Fig. 149. Phase diagram for tallow soap: (A) neat soap; (B) middle soap; (C) neat–middle–niger; (D) neat–middle; (E) middle–niger; (F) niger; and (G) neat–niger.[13] See text page 851.
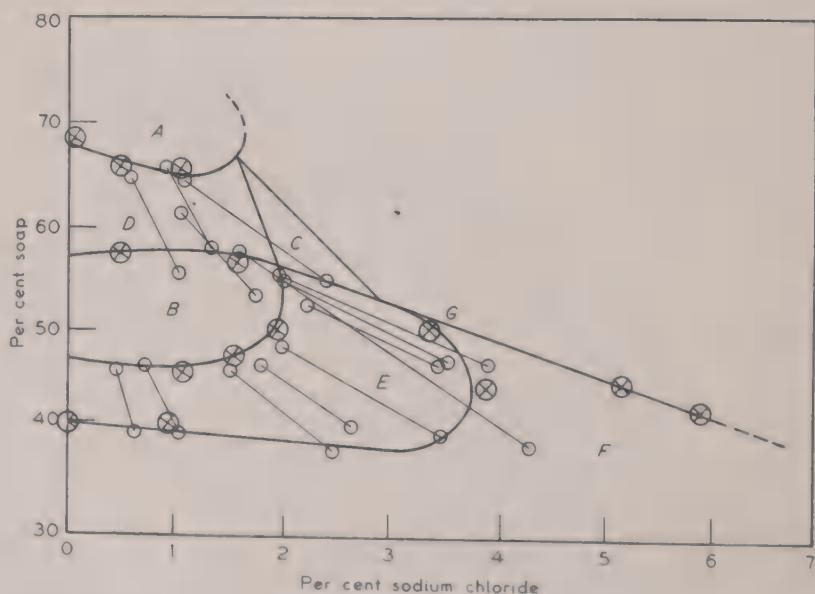
Fig. 150. Phase diagram for coconut oil soap: (A) neat soap; (B) middle soap; (C) neat–middle–niger; (D) neat–middle; (E) middle–niger; (F) niger; and (G) neat–niger.[13]
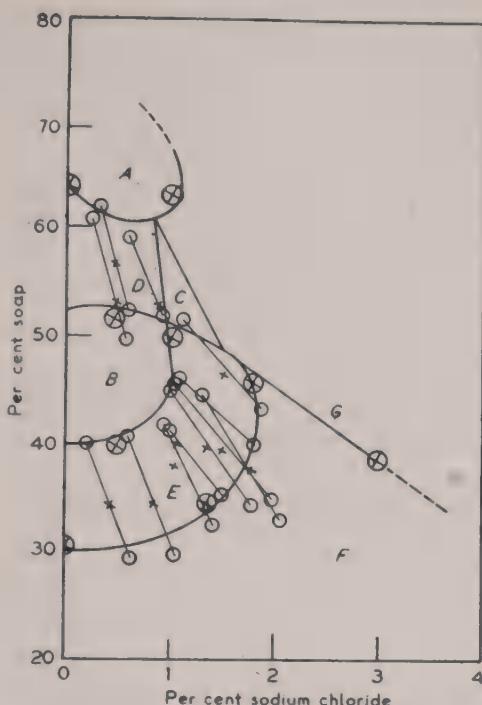
Fig. 151. Phase diagram for 75% tallow–25% coconut oil soap: (A) neat soap; (B) middle soap; (C) neat–middle–niger; (D) neat–middle; (E) middle–niger; (F) niger; (G) neat–niger.[13]
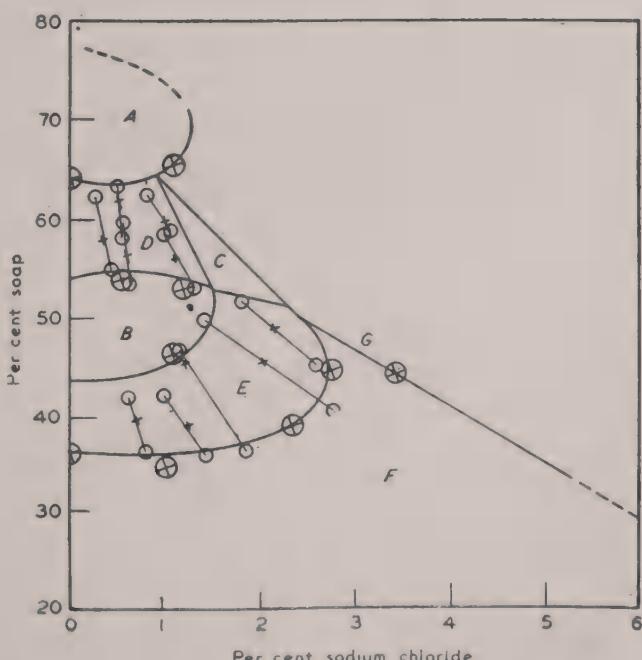
Fig. 152. Phase diagram for 50% tallow–50% coconut oil soap: (A) neat soap; (B) middle soap; (C) neat–middle–niger; (D) neat–middle; (E) middle–niger; (F) niger; (G) neat–niger.[13]

region, and again graining out as described above. The number of washes
given the batch is variable, but is ordinarily not less than two.

6. STRONG CHANGE

Before the soap-boiling operation is completed it is necessary to in-
sure that small proportions of neutral fat left from the killing change
are completely saponified. This is accomplished by the so-called "strong
change," which is carried out similarly to the washes described above,
except that graining out is accomplished with caustic soda rather than
lye, and the batch is given a prolonged boiling. No recovery of glycerine
is accomplished in this change; the "half-spent" lye resulting from the
operation is used for the saponification of fresh batches of fat.

7. FINISHING OR FITTING OPERATION

The final step in soap boiling is the so-called "fitting" operation,
sometimes referred to as "pitching" or "finishing." The finishing change
may follow the strong change directly or another brine change may be
interposed, if it is desired to make the free alkali content of the finished
neat soap very low, at some expense to its salt content.

In finishing, the soap is closed, by boiling with water as before, and its
content of water and electrolyte is so adjusted that the composition of
the system is brought into region F (Fig. 148), for example to the point
z. Upon standing the batch will then separate into an upper layer of neat
soap and a lower layer of thinner niger. In the example, the composition
of these is represented by the points z' and z'', respectively. The princi-
pal object of the separation is purification of the neat soap; the niger
retains most of the dirt, coloring materials, metallic salts, and other un-
desirable impurities of the batch, as well as much more than its share of
dissolved salt or free alkali. It will be seen from the diagram that the
portion of the neat soap boundary adjacent to area F is narrow and
relatively flat; hence with a given stock, the composition of the neat soap
can vary but little. In most commercial soaps the real soap content is
in the neighborhood of 65–66%. On the other hand, the composition of
the niger and the relative amounts of neat and niger can vary widely.
The fitting operation is thus highly critical and requires the utmost skill
upon the part of the soap boiler. The very narrow limits within which
he must work are evident from the diagram. The addition of but slightly
too large an amount of water or salt will produce too large a niger, and
diminish the yield of neat soap. If too little water or salt is added, too
small a niger may be produced, and purification may be short of that
desired. Furthermore, by the addition of water not greatly in excess of
the proper amount, by the use of insufficient salt, or by failure to mix it

the water thoroughly as it is added, the batch may be brought into regions *G* or *E*, with the formation of lumps of middle soap. Ordinarily, a niger is taken off which amounts to about 20–25% of the kettle contents and which contains about 30–40% soap. Upon settling, the niger layer tends to become higher in soap content at the top than at the bottom whereas the neat layer remains substantially uniform in composition throughout.

The phase boundaries are considerably altered by changes in the composition of the fat. The comparative phase diagrams of Ferguson and Richardson[13] for tallow soap, coconut oil soap, and mixtures of the two are shown on pages 848–849. It is to be noted that the areas of homogeneity and heterogeneity of the different soap phases extend over progressively wider concentrations of electrolyte as the percentage of coconut oil in the fatty stock increases. It is pointed out by the above-mentioned authors that this effect makes the accidental formation of middle soap more likely in the case of stocks containing large proportions of coconut oil than in the case of ordinary stocks. Considering the necessity for precisely determining the composition of the batch in order to make the pitching operation successful, and the variability in phase boundaries occasioned by unavoidable variations in the fat, it is understandable that soapmaking cannot be readily reduced to a series of mechanical operations, but must depend upon the skill and judgment of the experienced soapmaker, who is able to closely judge the progress of the operation by the appearance of the batch.

8. COUNTERCURRENT WASHING

Large plants having ample kettle capacity commonly use the so-called countercurrent wash system, to reduce to a minimum the amount of water to be evaporated in the recovery of glycerine. In the operation of this system only the spent lye of high glycerine content produced by the killing change is pumped directly to glycerine recovery; the weaker lyes from succeeding changes are used repeatedly for washing and are pumped from kettle to kettle in such a manner that they pass countercurrent to the soap mass, being progressively enriched in glycerine content in the process. For maximum glycerine strength in the spent lye it is also necessary to incorporate the niger from a previous batch during one of the washes rather than using it to aid saponification of the fresh fat.

According to Govan,[14] who has published a detailed description of the process, the countercurrent system will afford a 95% recovery of the theoretical amount of glycerine available, with a ratio of less than one pound of spent lye produced per pound of fat saponified.

[13] R. H. Ferguson and A. S. Richardson, *Ind. Eng. Chem.*, *24*, 1329–1336 (1932).
[14] W. J. Govan, Jr., *Oil & Soap*, *23*, 229–235 (1946).

9. Kettle Soap from Fatty Acids

There is a considerable manufacture in the kettle of soap from fatty acids, particularly of textile and other specialty soaps. Where fatty acids are used as the fat stock, saponification may be effected with sodium carbonate and, of course, no glycerine is recovered. Usually a strong (nearly saturated) soda ash solution is brought to a boil in the soap kettle, and the fatty acids are added gradually, with sufficient time being allowed between additions for carbon dioxide to escape without the batch foaming over. After the fatty acids are neutralized, the batch must be boiled with an excess of caustic soda, to saponify the small amount of neutral, unsplit fat which is present in all but the better grades of distilled acids. This treatment corresponds exactly to the "strong change" in ordinary soap boiling, and subsequently the batch is finished as described previously.

Soap made exclusively from fatty acids is reputed to be less firm than soaps made from the corresponding fats; the reason for this is obscure.

10. Curd or Boiled-Down Soaps

In a variation of the full-boiling process, the fitting operation is omitted and the soap is grained out with salt after the strong change, and then boiled down with closed steam coils until the salt content of the lye is quite high, e.g., until the hot lye tests about 20–25° Bé. This brings the composition of the batch considerably to the right of area M in Figure 148, and produces lye in equilibrium with the curd area indicated at the extreme upper left of the diagram. Upon drawing off the lye a curd soap will be obtained with an anhydrous soap content considerably above that of neat soap. This method is principally used for the manufacture of cheap soaps from inferior materials, as it provides a means of making a relatively hard soap from vegetable oil foots or low-titer greases.

Rosin cannot well be used in boiled-down soaps, nor can these soaps be blended with any considerable amount of soap builders, although 1–2% of sodium silicate is often worked in, principally for its antioxidant action.

11. Miscellaneous

(a) Soap Boiling Using Rosin

In the manufacture of yellow laundry soaps, or other soaps containing rosin, the rosin is either saponified separately, or added after the glycerine has been removed by the first brine changes. Rosin of course contributes

no glycerol to the spent lyes, and it is considered to "hold up" glycerol, if present in the first stages of saponification.

(b) Time Required for Soap Boiling

The total time required for preparing a batch of full-boiled soap is usually about 5–10 days; it varies according to the number of changes carried out, the size of the kettle, and whether rosin is included in the formula. In the first changes, about 4–8 hours are usually allowed for boiling and 4–16 hours (overnight) for settling. After fitting the batch is usually settled for not less than 2 days, and in some cases as long as 5 days.

It would obviously be desirable if soap boiling could be conducted with full control of the quantity of materials in the batch, with the success of the operation depending less upon the personal judgment of the soap boiler. Although many efforts have been made to introduce systems of quantitative control, these have not met with great success.

Wigner,[15] in particular, has treated this aspect of soap boiling at length, and has described methods for the control of both washes and fit, using a back-pressure, liquid level gage to estimate the weight of the kettle contents. According to Govan,[14] this method of weight estimation is generally accurate to with $\pm 2\%$, and is of real assistance in regulating the size of the washes.

(c) Bleaching in the Kettle

Soap is often bleached with sodium hypochlorite or other chemical agent in the kettle, preferably after the batch has been purified as much as possible by several "washes." Bleaching is carried out after water has been added to the curd to form a solution, and the soap is again grained out after the bleaching is completed.

(d) Purification of Nigers

As the impurities in the soap batch tend to accumulate in the niger, the latter cannot be used indefinitely for addition to fresh batches without purification. Purification of the niger can be accomplished by boiling and either "pitching" or salting out.

C. Semiboiled and Cold Processes

The semiboiled and cold processes represent soapmaking in its simplest form, wherein the fat is caused to react with a quantity of strong alkali very nearly equal to that just required for complete saponification, and

[15] J. H. Wigner, *Soap Manufacture*. Chemical Pub. Co., Brooklyn, 1940.

the entire mass is solidified without separation of the free glycerine and without separation of neat and niger phases. These processes have the advantage of requiring simple equipment and comparatively little skill on the part of the soapmaker, and a soap may be produced with an anhydrous soap content of any desired value over a wide range. On the other hand, they do not permit recovery of the relatively valuable glycerine, the raw materials do not undergo the purification obtained by the full-boiled process, and the product is generally considered somewhat inferior to settled soaps.

The two processes are used principally for making marine or other coconut oil soaps, which are difficult to handle by the full-boiled process, for making soft or potash soaps (which cannot be easily salted out), and for relatively cheap and heavily filled soaps made in small plants.

1. Semiboiled Soaps

Semiboiled soaps may be made either in an ordinary soap kettle or in small batches in a crutcher (see Sect. F1). In either case, the fat charge is simply heated with the requisite amount of strong caustic soda (25–35° Bé.), and after saponification is completed, sodium silicate or other builder or nonsoap ingredient is added. If the operation is carried out in a kettle, the batch may be actually boiled, but if performed in a crutcher, the temperature must be kept a little below the boiling point, and mechanical agitation is depended upon to insure thorough mixing during the reaction. However, to make the finished material homogeneous the kettle batch must be cooled slightly and mixed by recirculation from bottom to top through a pump before it is solidified.

2. Cold-Made Soaps

Insofar as the operation is concerned, the cold process differs little from the semiboiled process as carried out in the crutcher, except in the temperature employed.

Mixing is carried out substantially at room temperature, so that little more than thorough emulsification occurs in the crutcher. Very strong lyes, 35–45° Bé., are employed: the emulsion of strong lye and fat formed in cold saponification is said to be of the water-in-oil type,[7] as distinguished from the oil-in-water type produced in soap boiling. Saponification is completed after the soap is run into frames, several days at a reasonably warm atmospheric temperature being required for completion of the process.

Since there is no opportunity in the manufacture of cold-made soaps to adjust the proportions of fat and lye according to the reaction of the two, the charge must be quite carefully calculated. However, these soaps

usually contain a substantial excess of either alkali or, more commonly, fat. Any addition of builders, perfumes, or coloring material to cold-made or semiboiled soaps must of course take place in the crutcher.

Semiboiled and cold-made soaps are frequently prepared from fatty acids, as well as from fats.

D. Continuous Saponification

To avoid the time-consuming operations and excessive steam consumption of conventional soap boiling, a number of continuous saponification processes have been devised, and some are now being used commercially, on a very large scale. Certain of the continuous processes appear to be more suitable for the manufacture of laundry soap products, including the popular granular forms (which constitute the bulk of the total soap production), than for high-grade toilet soaps.

1. MILLS PROCESS

The first continuous saponification process to be operated on a large scale is that patented by Mills.[16,17] It involves, as a first step, splitting of the fat stock to produce fatty acids. The acids are then purified by distillation, which takes the place of washing and the separation of neat soap and niger, for the removal of color bodies and other impurities. The complete Mills process, as actually carried out in the soap plant, has been outlined by McBride,[17a] from whom the following description is largely taken.

In small batches the blended fat stock is mixed with a small amount of powdered zinc oxide and held at 220°F. The zinc oxide, which acts as a catalyst for hydrolysis, is soluble in the somewhat acid fat at this temperature, forming zinc soaps. In a second feed tank water is maintained at 200°F.

High-pressure pumps of the piston type pick up fat and water separately, at controlled rates. Beyond the pumps the two streams, under a pressure of 600 pounds, are heated to 495° and 480°F., respectively, by the direct injection of 900-pound steam. The fat is fed at the base and water at the top of a hydrolyzer column, also at 600 pounds pressure. This column consists of a 65-foot tower, without packing or baffles, in which most of the splitting takes place. The superheated water falls to the bottom of the tower in countercurrent flow to the hot fatty material, carrying with it the glycerol resulting from splitting of the latter. A time of 90 minutes in the apparatus is said to be sufficient for better than 99% splitting. Owing to the great solubility of water in fats and fatty acids at the high temperature employed (of the order of 12–25%), and the relatively slight difference in the density of the water and fat phases, elaborate measures for interdispersion of the two phases at any stage are unnecessary.

[16] V. Mills (to Procter & Gamble Co.), U. S. Pat. 2,156,863 (1939).
[17] V. Mills (to Procter & Gamble Co.), U. S. Pat. 2,159,397 (1939).
[17a] G. W. McBride, *Chem. Eng.*, *54*, No. 4, 94–97 (1947).

The "sweet waters" at the bottom of the tower are released through a pressure-regulating valve to a flash chamber and a multiple-effect evaporator, where they are concentrated to yield crude glycerine. The water-saturated fatty acids at the top of the tower are similarly released to a flash tank, where the temperature is reduced by flashing off of the dissolved water. From the flash tank the crude acids pass to a tank which feeds the distillation equipment. In this tank they are protected from the air by a blanket of steam.

Prior to being fed to the still, the fatty acids are heated to about 460°F. in a Dowtherm heater. Distillation is carried out under a pressure of 2–5 mm. The still may consist of a tray and bubble cap tower, down which the crude acids flow, with the unhydrolyzed fat being taken off at the bottom, or of a pot still of special design. In the latter case, a large proportion of the still bottoms is continuously recirculated through the Dowtherm heater to assist in maintaining the temperature in the still, and a minor proportion is continuously withdrawn, to maintain the concentration of unsplit material in the still at a fixed level. The still bottoms are reworked in a second processing stage, or are diverted to soap kettles for use in soap powders or lower-grade products.

The construction of the hydrolyzing and distillation equipment is of stabilized stainless steel where high pressures or temperatures are involved, and of aluminum where pressures are low.

The fatty acid distillate, cooled to about 180°F., is continuously fed, together with caustic soda solution, with proportioning pumps to a high-speed mixer, where saponification takes place almost instantaneously. The strength of the caustic soda is so adjusted that the composition of the product falls in the range of ordinary neat soap, and sufficient salt is added to the caustic soda to give a soap of the customary electrolyte content. Following this operation, the neat soap is processed into various forms in the usual way.

One of the prime advantages of the process involving splitting before saponification is its great flexibility. Stocks difficult or impossible to bleach satisfactorily can be distilled to yield light-colored fatty acids, and the manufacturer is not limited to a product having the composition of neat soap, but may produce a soap directly of substantially lower moisture content. This may be highly advantageous, as many commercial products (floating soaps, toilet soaps, spray-dried products) are marketed with a moisture content lower than that of neat soap. Furthermore, potash soaps of high purity can be prepared as readily as sodium soaps. The Mills process is said to produce soap products, including high-grade toilet soaps, which are fully equal in quality to those made by the best soap-boiling practice. There are complete plants employing the process which have no soap kettles.

2. SHARPLES PROCESS[18]

The recently introduced Sharples centrifugal soap process—which appears to be gaining wide acceptance—embraces the conventional soap-

[18] See U. S. Pat. 2,300,749 (1942), assigned by A. T. Scott to The Sharples Corp. and subsequent patents similarly assigned by various patentees, including particularly U. S. Pats. 2,397,161–162 (1946). L. Sender and L. D. Jones. See also J. C Smith, Chem. Inds., 63, 786–790 (1948); G. A. Frampton, Soap, Perfumery & Co-

boiling steps of saponifying, washing, and fitting into neat soap and niger. However, all steps are accomplished rapidly and continuously by separating soap and lyes and neat soap and niger with the aid of high-speed centrifuges. Less than two hours is consumed in converting the fat stock
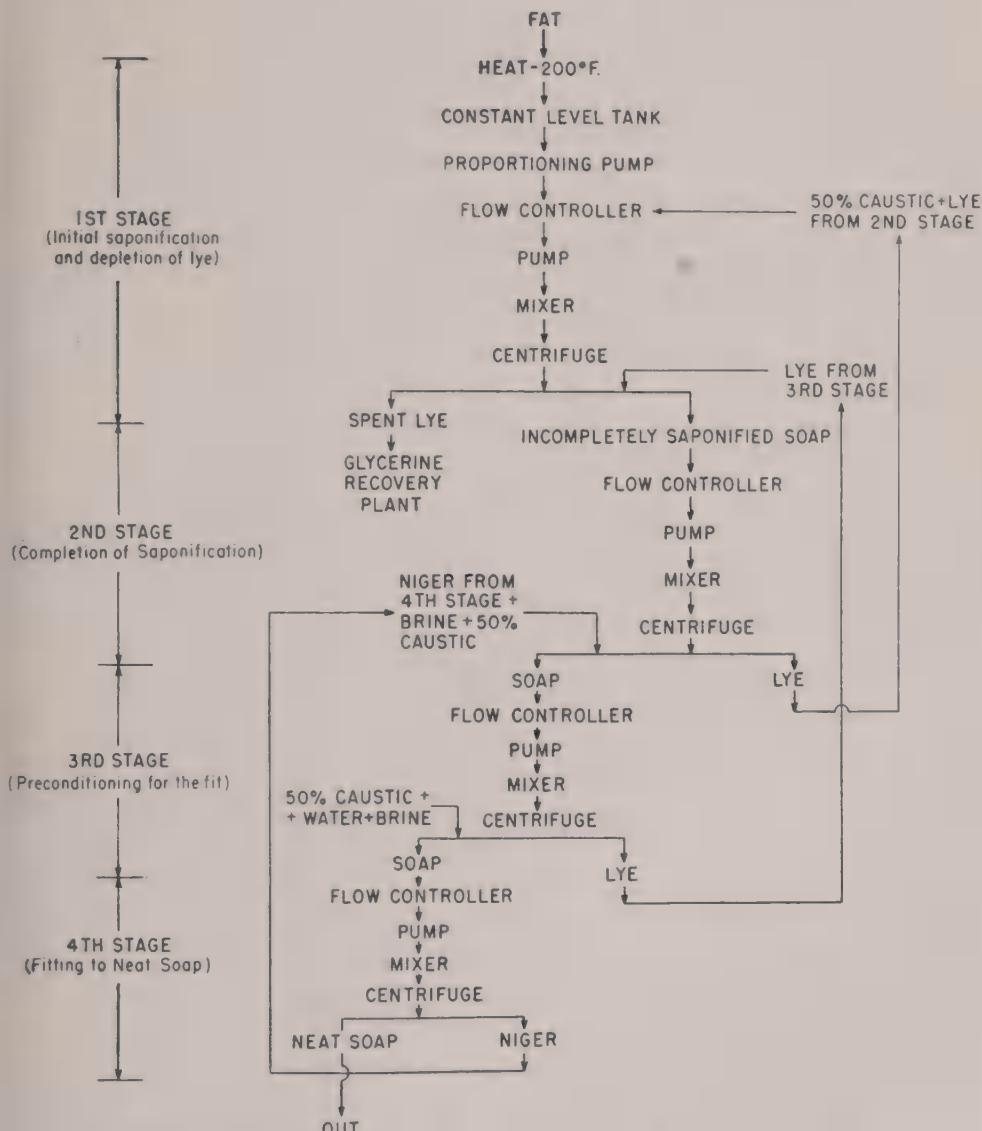
Fig. 153. Flow diagram for Sharples continuous centrifugal soap process (courtesy *The Sharples Corp.*).

to neat soap, and the steam consumption, amounting to about 0.17 pound per pound of fat processed, is but 15–20% of that of soap kettles. The ratio of spent lye to fat saponified (0.5–0.7 pound to 1 pound) is sub-

stantially less than that achieved in the best batch countercurrent washing practice (see page 851), and as the niger is continuously recycled, only neat soap and spent lye are discharged. The neat soap is said to be equivalent in soap, glycerol, free alkali, and salt content, and superior in color to that obtained by conventional boiling. In addition to being concentrated with respect to glycerine content, the spent lye is low in salt content (8–12%) and free alkali (0.1% or less Na_2O).

The flow of materials in the Sharples process is illustrated in Figure 153, which is largely self-explanatory. It will be noted that there are four stages of processing, which include three stages of saponification and washing and a final stage of fitting. With the use of automatic flow controls and interlocking proportioning pumps, accurate control of the entire process is achieved by periodically checking the caustic content of the lye at a single point in the system. Standard plants have capacities (in terms of fat processed) ranging from 1500 to 13,500 pounds per hour, in multiples of 1500 pounds.

3. Other Processes

Two other continuous soapmaking processes have apparently found somewhat limited commercial use. The first of these, the Clayton process,[19] is a short-time, high-temperature process, in which the fat and caustic soda are mixed and rapidly saponified (within about 5 minutes) while they are pumped through a heating coil. The soap, issuing from the coil at about 550°F., is sprayed into an evacuated chamber, where free glycerol is flashed off and recovered, together with almost all of the moisture. Mattikow and Cohen[20] have shown that serious decomposition of the glycerol in contact with alkali does not occur under the conditions of time and temperature that are employed. The hot dehydrated soap passes through a water-cooled screw conveyor, which forms a plug and seals the vacuum chamber, into a section where it is rehydrated to the desired moisture content with steam, and through a cooler, from which it issues in a form suitable for plodding. The second process, the French Monsavon process,[21,22] is generally similar to the Sharples, except that phase separations are carried out by gravity settling in a multiple decanter system, and a final stage of neutralization with fatty acids is required to produce a soap low in free alkali. The process is automatically controlled with respect to completeness of saponification through measurements of the

[19] See various U. S. Pats. of B. Clayton, B. H. Thurman, *et al.* (to Refining, Inc.), including the following—1,968,526 (1934); 2,019,775 (1935); 2,037,006 (1936); 2,123,647 (1938); and 2,283,776 (1942); and also M. Mattikow, *Oil & Soap*, **17**, 184–188 (1940).
[20] M. Mattikow and B. Cohen, *Oil & Soap*, **20**, 135–136 (1943).
[21] M. J. Seemuller, *Ind. corps gras*, **3**, 47–53 (1947).
[22] E. T. Webb, *Soap, Perfumery, and Cosmetics*, **22**, 483–486 (1949).

turbidity of a 15% soap solution, and of free alkali content, through similar photoelectric examination of the finished product to which alcoholic phenolphthalein has been added.

Other continuous saponification processes which are of some interest, but which have not attained commercial importance, include saponification to produce substantially anhydrous soaps in high-boiling petroleum naphtha or other inert solvent, followed by flashing off of the solvent and glycerol,[23] and saponification of methyl esters of the fat, followed by recovery and recycling of methyl alcohol, to react with fat to produce new esters.[24]

E. Glycerol Recovery

The recovery of glycerol from spent lyes is an important operation in any soap plant, as glycerol is an important by-product of soapmaking

The spent lyes contain, in addition to about 5–15% glycerol, a considerable and variable quantity of salt, a small amount of free caustic soda, traces of dissolved soap, and certain organic impurities derived from the fat. The first step in glycerol recovery is treatment of the lye with aluminum sulfate and sulfuric or hydrochloric acid. The addition of about 4 to 14 pounds of aluminum sulfate to each 1000 pounds of lye precipitates any dissolved soap in the form of insoluble aluminum salts, and reacts with the excess caustic soda to form a flocculent precipitate of aluminum hydroxide which has a high adsorptive capacity for albuminous material or other organic impurities. Sufficient acid is also added to neutralize any caustic soda remaining after reaction with the aluminum sulfate. After treatment is completed the clarified lye is filtered in ordinary filter presses.

The treated lye is evaporated to precipitate the bulk of the salt, and concentrate the solution to so-called 80% crude glycerine. Vertical-tube, double-effect evaporators are commonly used for evaporating the solution to a glycerol concentration of about 40%, at which point it is known as "half-crude" glycerine. Separation of the bulk of the salt occurs in the second effect, the salt settling to the bottom of the evaporator and thence falling into salt drums. Valves are placed in the pipes leading from the evaporators to the salt drums, so that the latter may be periodically cut off from the evaporator proper, and emptied. The recovered salt, after washing and drying, is reused for salting out new batches of soap.

In the further concentration of half-crude to 80% crude glycerine, the

[23] See V. R. Kokatnur, U. S. Pat. 1,813,454 (1931); J. K. Gunther (to Industrial Patents Corp.), U. S. Pat. 2,401,756 (1946); P. Bradford (to Swift & Co.), U. S. Pat. 2,496,576 (1950).
[24] G. B. Bradshaw and W. C. Meuly (to E. I. du Pont de Nemours & Co.), U. S. Pat. 2,271,619 (1942). G. B. Bradshaw, U. S. Pats. 2,452,724–5 (1948).

first effect is cut out of the system, or a separate single-effect evaporator is used, high-pressure steam being employed in either case for heating the solution. With the usual vacuum of 26 to 28 inches on the evaporator, a concentration of 80% will be reached when the temperature has risen to about 190° to 200°F.; excessive losses of glycerine will occur if further concentration is attempted.

Ordinary 80% crude glycerine contains a considerable amount of salt, and various other impurities, both organic and inorganic. Purification and further concentration of this product, to yield the commercial grades of c.p. glycerine, u.s.p. glycerine, dynamite glycerine, etc., is carried out by fractionally distilling the glycerol from the nonvolatile impurities under vacuum, with the aid of superheated steam, and treating the distilled product with bleaching carbon and various chemicals.

Modern techniques in the purification of spent lyes and recovery of glycerine are treated in detail in the treatise of Thomssen and McCutcheon,[2] and in articles by Govan[25] and Peterson.[26]

F. Transformation of Molten Soap to Finished Forms

1. CRUTCHING

If neat soap from the kettle is to be blended or mixed with builders or other materials before it is framed or dried, the blending operation is carried out in machines known as crutchers. These consist of small cylindrical vessels, usually of about 1500–5000 pounds capacity, which are equipped with agitators designed for handling heavy materials; the most common agitator consists of a spiral screw which lifts the material upward through a cylindrical draft tube suspended in the vessel. Crutchers are also generally used for mixing caustic and fat in the manufacture of cold-made soaps, and are sometimes jacketed and used for remelting and reworking scrap from framing, although special remelting tanks discharging into the crutchers are more commonly provided.

2. MANUFACTURE OF FRAMED SOAPS

The simplest method of converting neat soap, or other hot liquid soap to a solid form suitable for forming into bars, is known as framing. This consists simply of running the liquid soap (at 135–145°F.) into portable frames and allowing it to solidify spontaneously in the form of large cakes. In Europe there is a considerable use of water-cooled devices in which the soap is solidified rapidly in the form of thin slabs, but these have never become popular in the United States.

[25] W. J. Govan, Jr., Oil & Soap, 21, 271–275 (1944).
[26] W. A. Peterson, J. Am. Oil Chem. Soc., 24, 79–84 (1947).

The frames consist of a bottom, mounted on wheels, and four removable sides, which can be clamped together to form a liquidtight compartment, and yet be readily removed from the solidified cake. A frame of soap usually weighs 1000 to 1200 pounds, and is shaped in the form of a high, narrow rectangle, for maximum convenience and economy in subsequent cutting operations. From 3 to 7 days are required for the solidification of neat soap; cold-made soaps may require slightly longer, since saponification is completed in the frames.

The frames of soap are cut into slabs and then into cakes by being forced through metal frames set with thin, taut wires. The cakes or blanks resulting from this operation must be dried to some extent before they can be stamped and wrapped. Drying is carried out by passing the blanks through drying rooms or tunnels, where they are subjected to the action of warm, dry, circulating air. Drying occurs largely on the surface. hence the moisture content of the whole bar is not usually reduced by more than 3 to 5%.

Floating soaps produced by framing simply contain a considerable proportion of air beaten into the soap mass in the crutcher. This air is in the form of very fine, almost invisible bubbles, which are readily retained by the viscous soap entering the frames.

Added materials, such as builders, antioxidants or stabilizers, perfumes, etc., are crutched into the kettle soap before framing.

3. Manufacture of Chips and Flakes

Soap chips are manufactured not only to be packaged as such, but also to be milled and plodded into toilet soap bars, the solidification and drying of soap in the form of chips having in modern plants entirely supplanted other methods of preparing neat soap for milling.

Solidification of soap for the production of chips is accomplished on a chilling roll, about 4 to 5 feet in diameter, and twice to three times as long, cooled internally by the circulation of water. The molten soap, which may be pure neat soap if the chips are to be milled, or a mixture of neat soap and builders if they are to be packaged for home laundry use, is picked up or discharged onto the surface of the roll, where it is spread into a thin and uniform layer by the action of a smaller feed roll set above the chill roll, with only a slight clearance between the two. The soap, solidifying as the roll slowly revolves, is marked off into narrow ribbons by a series of needle points bearing against the roll surface, and is thereafter removed from the roll by a scraper blade.

The soap ribbons fall from the chill roll onto a wire mesh conveyor, which carries them slowly back and forth through a tunnel dryer heated by steam coils and provided with forced circulation of air. By regulating

the temperature within the dryer, and the speed with which the conveyor operates, the moisture content of the material may be quite accurately controlled, about 13–14% moisture being desired in a product which is to be milled. The ribbons taken from the chilling roll naturally break up into chips in subsequent handling, after they have dried sufficiently to become brittle. Care is exercised in drying to avoid heating the chips enough to cause them to melt partially and stick together or adhere to the conveyors.

Chips taken hot from the dryer cannot be packaged or stored directly; hence the final stage of the drying operation consists of circulating cool air through the material to reduce its temperature.

Milled flakes are made only from pure soap, with no builder added, and are the highest grade and most expensive form of the various quick-dissolving soap products. They are produced by repeatedly milling dried chips of relatively low moisture content (about 10–11%) through special, close-set, water-cooled steel rolls. Drying of these flakes to a brittle form is actually accomplished on the rolls, and the flakes are ready for packaging after milling is completed. A very thin flake is produced, which has a distinctive polished appearance and the quick-dissolving characteristics of milled soap in the bar form.

4. Manufacture of Other Quick-Dissolving Forms

(a) Spray Drying

Spray drying has very largely supplanted older comminution processes for the production of soaps in a finely divided, quickly dissolving form. It is used for the preparation of both pure soap products and those which include moderate proportions of builders.

This process consists, in the simplest terms, of forcing the molten soap through spray nozzles in the top of tall towers, the small particles thrown out by the nozzles becoming solidified and drying as they fall through a parallel or countercurrent stream of heated air.

The process is subject to many variations having to do with the temperature and composition of the liquid soap, the temperature and flow of air within the tower, and the mechanical devices used for forming the spray, all of which have their effect on the characteristics of the finished product. However, data on the actual operation of the different processes are not generally available.

Spray-dried soap products have become very popular in recent years, and have to a considerable extent replaced soap chips and bars for general household use. The object in preparing a spray-dried product for household use is to obtain a material composed of uniform particles which are thin and easily dissolved, yet not excessively bulky or dusty.

Some puffing of the soap particles occurs and this must be carefully controlled, through attention to the spraying devices and the temperature, velocity, and direction of air flow, to produce particles that are thin-walled and possessed of the proper bulk density. Fine particles entrapped by the air stream are caught by dust-collecting equipment and reprocessed.

(b) Mechanical Reduction

The mechanical reduction of soaps to powdered form is relatively little practiced since the advent of spray-drying processes, although it is still necessary to grind soap powders for special purposes, particularly for the manufacture of shaving powders, dentifrices, and certain other toilet goods.

It is necessary to dry soap chips to a very low moisture content, i.e., below about 3%, in order for them to be sufficiently pulverulent to grind well. Chips of this low moisture content will under most atmospheric conditions absorb moisture from the air; hence the dried chips must be immediately ground, or stored without free access to the air. The chips ground for toilet purposes consist only of very pure soap made by the full-bodied process.

Reduction of the dried chips is carried out in attrition mills, which are equipped with air separators to separate the finer particles and recycle coarser particles to the feed. An open circuit, with a constant throughput of cooling air is recommended, to avoid overheating the powder. Some degree of drying is also accomplished in an open circuit, the finished powder often containing as much as 99% of anhydrous soap.

5. Manufacture of Milled Bars

High-grade toilet soap bars are almost invariably milled. Milling and plodding of partially dried soap chips into bars accomplishes several objects which cannot be attained by simply allowing neat soap to solidify in frames. By this process the moisture content of the soap may be reduced to less than 15%, whereas that of framed soap will hardly be less than about 30%. The working undergone in the rolls produces a certain degree of orientation of the crystalline soap fibers, which contributes to the distinctive physical properties of the product. Also this working converts the soap largely to the beta-phase, as contrasted with the omega-phase principally existing in framed soaps. The milling process permits the addition of perfumes after the soap has become cold; hence perfumes may be used which are unstable in the presence of hot alkalies or are relatively volatile.

The recommended moisture content of chips which are to be milled is

between about 13 and 14%. Chips of much lower moisture content are difficult to mill properly, whereas those of high moisture content are too gummy and soft to mill well or to handle well in the plodders, cutters, and presses.

The first operation in the manufacture of milled soaps consists of mixing weighed batches of chips in amalgamators, or heavy horizontal mixers, with perfume, dyes, titanium dioxide, or other whitening material, etc. From the amalgamator the mixture is transferred to the mills. These consist of a series of rolls through which the soap mass is passed in the form of a thin sheet. The individual rolls rotate at different speeds, so that the sheet, in passing between adjacent rolls, is not only compressed, but also subjected to an intensive shearing action. The soap is stripped from the last roll in the form of thin ribbons, as in the preparation of soap chips.

Milling rolls were formerly made only of stone, granite being the preferred material for their construction, but now they are commonly made of chilled iron. Iron rolls are made in hollow form, and cooled by circulating water, which carries away the frictional heat generated in the soap during milling. Hence they may be run at a higher capacity than granite rolls without danger of overheating the soap.

Compression of the milled soap into a dense, coherent form, suitable for forming into bars, is accomplished in a plodder. This machine is not unlike an ordinary sausage grinder. It consists of a hopper communicating with a horizontal chamber of circular cross section, in which revolves a spiral compression screw. The soap mass is forced through a compression cylinder containing a plate with multiple perforations, and then extruded under high pressure through an orifice in the end or "nose" of the device in the form of a continuous bar. The compression cylinder is jacketed for the circulation of cooling water, and the nose is electrically heated. Passage of the bar of soap through the heated nose melts the surface just sufficiently to impart to it a high polish.

The extruded bar emerges to a cutting table where it is cut into blanks by a wire cutter. The blanks are stamped into finished soap bars in automatic presses fitted with dies bearing the lettering or design desired, and are then automatically wrapped.

There are certain variations of the above-described process. A preplodder is often placed between the milling rolls and the plodder. The preplodder is similar to the plodder except that the nose is omitted; hence it extrudes the soap in the form of small round rods, which are cut into pellets by a revolving cutter. Feeding of the plodder is facilitated by thus preforming the feed material. It is also possible to eliminate the milling rolls entirely by passing the soap through a succession of suitably designed preplodders equipped with orifice plates with small perforations.

Forcing of the soap through these small openings under high pressure provides a shearing action which accomplishes the same purpose as milling.

6. Continuous Solidification of Bar Soaps

The two popular American brands of floating soap are solidified continuously in equipment of special design, as a critical heat treatment combined with mechanical working is required to produce a finished bar in which the soap is largely in the easily dissolved beta-phase rather than the omega-phase characteristic of framed bars of equivalent moisture content (see page 353). In each case the material to be solidified is not neat soap, but soap containing about 20% moisture.

The patent which has been held to dominate the manufacture of beta-phase floating soaps was issued to Bodman[27]; published descriptions of the related process and apparatus are to be found only in the patent literature.[28]   The starting material consists of pellets from the soap plodder. These are heated to 160°F. or above and the hot plastic material is worked and aerated in a closed "converter," consisting of a jacketed vessel or barrel containing intermeshing screws. The material from the converter is discharged continuously to a special molding machine which forms it into a continuous bar and at the same time chills the surface of the bar sufficiently to make it form-retaining. The bar is then trimmed, cut, and, after further cooling and tempering, stamped and wrapped.

The second method of solidifying floating soap is described in a patent issued to Mills,[29] and also by McBride.[17a]   The starting material is neat soap, which is reduced to a moisture content of about 20% by being heated to 400°F. under a pressure of 700 pounds and sprayed into a flash chamber. The pasty and viscous material from the flash tank, at a temperature of about 220°F., is solidified and aerated to a density of about 0.8 in a special brine-cooled chilling machine similar to the Votator machine used for the solidification of plastic fats (see page 922). The solidified soap is extruded from the chiller onto a conveyor in the form of a continuous soft, but form-retaining bar, at a temperature of about 150°F. On the conveyor it is cut into lengths equivalent to three finished soap bars, which are transferred to trucks and further cooled before they are again cut and stamped. The temperature of extrusion is said to be rather critical; with soap made from 20% coconut oil and 80% tallow and having a moisture content of about 20%, a bar of the proper physical characteristics is obtained only between about 125° and 160°F.[30]

[27] J. W. Bodman (to Lever Bros. Co.), U. S. Pat. 2,215,539 (1940).
[28] See F. F. Pease (to Lever Bros. Co.), U. S. Pats. 2,048,286 (1936) and 2,373.593 (1945).
[29] V. Mills (to Procter & Gamble Co.), U. S. Pat. 2,295,594 (1942).
[30] Procter & Gamble Co., Brit. Pat. 555,034 (1943).

FRACTIONATION OF FATS AND FATTY ACIDS

A. Introduction

Oils, fats, or mixed fatty acids are fractionated to provide new materials more useful than the old. Often fractionation is carried out merely to rid a fatty material of minor quantities of an unwanted component. Such is the fractionation sought in the winterization of vegetable oils or fish oils. However, separation of fat or fatty acids into fractions will often provide two or more improved products from the same original material. Thus, for example, the pressing of tallow fatty acids yields commercial oleic and stearic acids, each of which have properties which render it more suitable for specific purposes than the mixed acids.

Although the fractionation processes in use at present consist principally of those which have been in operation for many years, some methods have been but lately introduced, and there is every prospect that fractionation may generally assume greatly increased importance in the future. In order to appreciate the potential utility of fractionation techniques it is necessary to recall that in very few cases can present oil and fat products be said to have completely satisfactory compositions. Most lard, shortenings, and margarine, for example, would possess greater stability and in consequence probably be better edible products if they contained smaller amounts of acids more unsaturated than oleic acid. On the other hand, most paint and varnish oils would be improved if they contained more of the highly unsaturated compounds which are undesirable in edible products, and lesser quantities of more saturated components. Soaps invariably contain fatty acids which could be eliminated to the improvement of their quality.

In some cases natural fats contain such a variety of fatty acids that this variety in itself constitutes a disadvantage. An excellent example of such unfortunate variety in fatty acid components is furnished by sardine oil and other fish oils. These oils contain large proportions of very highly unsaturated fatty acids, but also quite substantial amounts of completely saturated acids. The completely saturated acids prevent fish oils from being entirely satisfactory drying oils, and, on the other hand, the highly unsaturated acids make them relatively poor materials for the manufacture of edible products. It is not feasible at present to convert fish oil

into fractions consisting respectively of glycerides of saturated and mono-ethenoid acids, and glycerides of fatty acids with two or more double bonds, but if this could be done, the former would be entirely suitable for use in high-grade food products, and the latter would constitute an excellent drying oil.

The ultimate in fractionation has been outlined in a somewhat fanci-ful but illuminating article by Potts.[1] It would simply involve splitting the available oil and fat supply into glycerol and fatty acids, separating the latter into fractions comprising the individual acids or classes of acids and then diverting the latter to food, paint, soap, etc., according to their particular adaptabilities, either with or without previous re-esterification with glycerol, as might be required. Such a scheme for fat ultilization is of course fantastic in its over-all aspects, but it cannot be doubted that new "tailor-made" fats, prepared according to the principles outlined above, will henceforth find increasing use.

Fractionation can usefully be applied to both fats and fatty acids. How-ever, it is to be noted that in the case of fats, the degree to which the properties of the material may be modified is limited by the highly mixed nature of natural glycerides. The glycerides tend to assume the average characteristics of the fatty acids, since three different acids of diverse nature and properties may be combined within a single triglyceride mole-cule. If fractionation is carried out on the free fatty acids or their mono-esters, the attainable separation is limited only by the efficiency of the fractionation methods, and with the use of sufficiently effective techniques might conceivably be carried to the point of near quantitative separation of the individual acid or esters.

B. Fractional Crystallization

1. THEORY[2]

Components of a fat or fatty acid mixture that differ considerably in melting point, e.g., saturated and unsaturated acids, can be separated by crystallizing out the higher melting component. Most commercial frac-tional crystallization processes are carried out in a melt of the fatty material, rather than in a solution of an organic solvent, and only a rough separation is achieved; the difficulty of making a more complete separa-tion lies chiefly in the mechanical operation of removing crystals from the melt without excessive entrainment of liquid. By crystallizing from a solution and washing the separated crystals with solvent, mechanical en-

[1] R. H. Potts, Oil & Soap, 18, 199–202 (1941).

[2] For detailed information on the theory and practice of fractional crystallization, see R. S. Tipson, "Crystallization and Recrystallization," in Technique of Organic Chemistry, Vol. III, A. Weissberger, ed., Interscience, New York, 1950. See also A. E. Bailey, Melting and Solidification of Fats, Interscience, New York, 1950.

trainment may be largely obviated, and other advantages gained. In the presence of a solvent, equilibrium between the solid and liquid phases is established much more rapidly, large, easily separable crystals are produced even at relatively high cooling rates, and the viscosity of the liquid phase is reduced so that separation of the crystals by filtration or other means is more rapid. Also, if there is a tendency for mixed crystals to form, this tendency is generally reduced in the presence of a solvent. It is to be noted, however, that many fatty mixtures form eutectic systems, and that limitations upon separation imposed by the existence of a eutectic may be minimized, but are never eliminated by the use of a solvent. For example, in mixtures of stearic acid and oleic acid, it is impossible to increase the purity of the oleic acid in the liquid phase above about 97.5% by crystallizing out stearic acid, because of the eutectic at this composition.[3] In a solution of petroleum naphtha, the purity of the oleic acid similarly cannot be made greater than about 98.7%.[4]

The highly mixed nature of most natural glycerides precludes any very efficient separation with respect to saturated and unsaturated acids by fractional crystallization. However, it is possible to reconstitute fats and separate fractions of high and low degrees of unsaturation very effectively by fractional crystallization combined with interesterification, according to the "directed interesterification" technique of Eckey (see Chapter XIX).

2. WINTERIZATION OF VEGETABLE OILS

The process by which the higher melting glycerides are removed from oils is termed winterization, from the circumstance that separation was formerly carried out by simply allowing the oil to stand and settle out in outside tanks during the winter. The present large demand for such oil makes it necessary to employ artificial cooling, and filtration of the liquid from the solid portions.

Practically all of the winterized vegetable oil at present manufactured consists of cottonseed oil. Such oils as soybean, corn, sunflower, and olive oil do not require winterization to remain liquid at low temperatures (although corn and soybean oils must be cleared of waxes to prevent clouding), and it is not feasible to winterize peanut oil because of its tendency to deposit difficultly filterable crystals. Edible oils which will remain substantially liquid at temperatures of 40° to 45°F. are in particular demand in the United States because of the widespread use in this country of mechanical household refrigerators operating at these temperatures.

[3] J. C. Smith, *J. Chem. Soc.*, *1939*, 974–980.
[4] W. S. Singleton, *J. Am. Oil Chem. Soc.*, *25*, 15–20 (1948).

The problem of winterized oil manufacture resolves itself principally into a matter of producing crystals of a form that can be separated from the uncrystallized oil. This is a matter of some difficulty. At the relatively low temperatures required for crystallization the oil is quite viscous; the reluctance of substances to deposit well-formed crystals in viscous media is well known, particularly when the molecules forming the crystals are large, as they are in the case of triglycerides. The oil must be cooled with extreme slowness in order to produce filterable crystals, and even under the most favorable circumstances the final separation of solids and liquid is difficult and incomplete. Because of the slowness of the operation and the poor separations obtained, ordinary winterization is one of the least satisfactory of present oil processing methods.

It is customary to conduct the entire winterization operation in refrigerated rooms, although the chilling tanks may be placed in a room at atmospheric temperature if they are closed and well insulated. In some plants the chillers are built in a very narrow form (in some cases as little as 2 or 3 feet in width), to facilitate heat transfer from their interior, and refrigeration is applied through the cold air of the room. It is more usual, however, to employ tanks of conventional shape and size, and equip them with cooling coils. The direct expansion of a refrigerant in the coils can scarcely be depended upon to provide the gradual cooling requisite for proper crystal formation. They are usually designed, therefore, for the circulation of cold brine. It is more or less essential to have the refrigeration system so arranged that the temperature of the brine may be easily varied and positively controlled. In order to avoid shock chilling of the oil next the coils, the temperature differential between the brine and the oil should never be large. A differential varying from about 25°F. when the oil is at 75°F., to about 10°F. when the oil is at 45°F., is usually satisfactory. The coils must be quite closely spaced in the tank, as mechanical agitation of the oil to bring it into contact with the coils cannot be permitted after crystals have begun to form.

As stated previously, an absolutely essential feature of the process is a slow rate of chilling. Even when the greatest care is exercised in chilling, filtration of the cold, viscous oil from the relatively nonrigid crystals is a difficult matter, and carelessness in forming the crystals may easily lead to complete failure of the operation.

The following represents a typical sequence of operations in the preparation of a highly winterized cottonseed oil. The oil charged to the chillers at a temperature of 70° to 80°F. It is then cooled to 55°F. in 6 to 12 hours. At about this temperature the first crystals will appear in an average oil. The cooling rate is then reduced somewhat, and an additional 12 to 18 hours is allowed for the temperature to drop to about 45°F. The rate of crystallization will then be sufficiently rapid to cause a slight rise

in the temperature of the oil, even though the refrigeration input is maintained at a constant level. The temperature will usually rise 2° to 4°, and then drop as before. When it has dropped to a point slightly below the previous minimum (e.g., to 42°F.) the cooling is discontinued, and the batch is held at this temperature for a considerable time. The exact duration of this latter holding period will depend upon the degree of winterization desired. There will be progressive crystallization for an extended time after cooling has ceased, and the degree of winterization attained will depend much more upon the length of the holding period than upon the actual holding temperature. A holding period of 12 hours will generally insure a cold test (time required to cloud at 32°F.) of upward of 20 hours.

Filtration of winterized oils is usually carried out in ordinary plate and frame filter presses of large capacity. In order to convey the crystallized oil to the presses with the least possible disturbance and disintegration of the crystals, the chilled mass is usually dropped by gravity from the chillers into small closed pressure tanks, or "eggs," from which it is forced to the presses with compressed air. Low-speed rotary pumps of the positive displacement type are less commonly employed for the same purpose. If the chillers are of the closed type, and built to withstand moderate internal pressure, the oil may of course be transferred by air pressure directly from chillers to presses.

Considerable filtering capacity is required, as compared with ordinary filtering operations; the average rate of filtration in handling a complete batch may not exceed about 1 pound of oil per hour per square foot of filtering surface. Filtration must be conducted at a low pressure (about 5 to 20 pounds gage), as the application of high pressure will compress the filter cake and render it quite impermeable to the passage of oil. The time required for both crystallization and filtration of a batch will generally be 3 to 6 days, although some plants operate on an even longer cycle.

After filtration is completed and after the filter cake is removed from the presses, the cloths of the latter must be periodically heated to melt and remove the fat crystals clogging their pores. This is commonly accomplished by circulating warm oil through the presses.

The yield of winterized oil from cottonseed oil is ordinarily between about 75 and 85% oil with an iodine value of 110–114. The stearine or filter cake is relatively low in melting point, and hence cannot be substituted for hydrogenated stearine in the manufacture of shortenings, but is used in shortenings or other products to replace a roughly equivalent amount of cottonseed oil. Winterized stearine is considered a relatively low-grade product, presumably because it contains traces of waxes, gums, soaps, etc., which are precipitated from the refined oil upon cooling; hence it is usually blended in limited quantities into lower grade shortenings.

A large part of the filter cake consists of entrained oil rather than solid fat; actually, from average cottonseed oil of 108 iodine value, only 8–10% of crystals are removed in winterizing.[4a]

Occasionally oils will be encountered which fail to crystallize normally in the winterization process, even though they may be of ordinary glyceride composition. A peculiarity of this kind was observed, for example, by Ronzone[5] in the case of Chinese cottonseed oil. It seems probable that abnormal hibits of crystallization in otherwise normal oils are usually due to the presence in the latter of natural crystal inhibitors. On the other hand, the addition of lecithin, a crystallization inhibitor, to cottonseed oil before winterization has the effect of improving the filterability of the crystals.[6] The addition of oxidized oil products or other crystallization inhibitors (see page 199) to oils after winterization is quite common.

The standard cold test of the American Oil Chemists' Society requires that a winterized oil remain clear after 5.5 hours immersion in ice and water. However, most winterized cottonseed oils will pass such a test for 8 to 16 hours, and oils with a cold test of 20 hours or more are not uncommon. From a practical standpoint, the time required for an oil to cloud at 32°F. is less important than the amount and character of the crystals which the oil will deposit after a more prolonged holding period at a low temperature. Some manufacturers test their winterized oils by means of cloud and pour tests conducted by the A.S.T.M. method for lubricating oils. The cloud and solid points of an oil bear a more or less inverse relation to the time required for it to cloud at a low temperature. An oil with a cold test of 15 hours at 32°F., for example, will have cloud and solid points of about 24° and 20°F., respectively. Unwinterized cottonseed oil will usually become quite solid in 1 hour at 32°F., and will have respective cloud and solid points of about 36° and 28°F.

Soybean, corn, and linseed oils are often chilled to remove waxes which cause them to become cloudy at low temperatures, together with traces of gums, etc. However, the waxes are present in little more than traces (see page 28), and the oil may be chilled quite rapidly and filtered with relative ease. In some plants, filtration is carried out in ordinary cloth-dressed presses, with the assistance of a small amount of diatomaceous earth mixed into the oil before chilling. In others, no filter aid is used, but the filter cloth is covered with paper, which is discarded together with its gummy coating after filtration is completed.

Peanut oil has higher cloud and pour points than cottonseed oil (about

[4a] E. I. Skau, W. N. Dopp, E. G. Burleigh, and L. F. Banowetz, *J. Am. Oil Chem. Soc.*, *27*, 556–564 (1950).
[5] P. E. Ronzone, *Oil & Soap*, *13*, 165–167 (1936).
[6] L. C. Brown (to Industrial Patents Corp.), U. S. Pat. 2,393,744 (1946); see also C. M. Gooding and J. R. Rich (to Best Foods, Inc.), U. S. Pat. 2,435,626 (1948).

40° and 34°F., respectively), but the virtual impossibility of winterizing this oil appears to arise from its tendency to form peculiarly gelatinous and nonfilterable crystals, even when chilled very slowly, rather than from its containing any excessive proportion of solid material.

In a solvent such as hexane or acetone, cottonseed oil can be readily winterized to produce a better oil in a higher yield than is obtained in conventional winterization.[4a,7] Furthermore, the total chilling and holding time required (1.5 hours or less) is such as to make continuous operation practicable. However, the relatively high cost of continuous filtration and solvent-handling equipment, and the limited output of most plants, has thus far prevented commercial application of the process. The Emersol process for the fractional crystallization of fatty acids, using methyl alcohol as a solvent, is said to be applicable to the winterization of vegetable oils, as well as the fractionation of other fats and oils.[8]

3. COLD CLEARING OF FISH OILS

Fish oils intended for use in paints or other protective coatings are usually winterized to remove relatively saturated glycerides which interfere with the drying of the oils to hard, nontacky films. Cod liver oil or other medicinal oils may be winterized simply for the sake of the appearance of the oil in cold weather.

According to Behr,[9] a sardine oil winterized for use in paints or varnishes should have a clouding time at 32°F. of not less than 14 hours. This writer observed that it was necessary to remove approximately 30% of high melting material from sardine oil to produce oil with a cold test of 20 hours, the saturated acid content of the oil (by the Twitchell method) being decreased from 22 to 17% in the process. Further winterization, to increase the cold test of the oil to 90–100 hours, reduced the saturated acid content only to 16.75%. Another lot of winterized sardine oil with an iodine value of 203.5 and a cold test of 40 hours was found to contain 17.5% of saturated acid. Winterization of the oil not only caused it to polymerize more rapidly in the operation of heat bodying, but also made it more reactive with phenolic resins.

Brocklesby[10] reported that in a laboratory experiment a temperature of 34°F. was required to remove 21.8% of high-melting glycerides from pilchard oil, the saturated fatty acid content of the oil being reduced to

[7] A. E. Bailey, R. O. Feuge, E. A. Kraemer, and S. T. Bauer, *Oil & Soap*, *20*, 129–132 (1943).

[8] R. E. Kistler, V. J. Muckerheide, and L. D. Myers, *Oil & Soap*, *23*, 146–150 (1946).

[9] O. M. Behr, *Ind. Eng. Chem.*, *28*, 299–301 (1936).

[10] H. N. Brocklesby, *The Chemistry and Technology of Marine Animal Oils*. Bull. No. 59, Fisheries Research Board of Canada, Ottawa, 1941.

17.0%. However, in the winterization of fish oils, as in that of cotton-seed oil, it would appear that the degree of winterization obtained should depend more upon the holding time at the minimum temperature than the actual temperature employed. In another experiment Brocklesby found that various pilchard and sardine oils deposited 17–32% of solid glycerides during a 24-hour holding period at 48°F.

The equipment and technique employed in winterizing fish oils are not essentially different from those described above in connection with the winterization of cottonseed oil, although in the case of fish oils there is a somewhat more clean-cut fractionation of the oil on the basis of the iodine values of the fractions, and somewhat more rigid and easily filterable crystals are obtained.

4. Fractional Crystallization of Animal Fats

The fractional crystallization of oleo stock (beef fat) to produce oleo oil and oleostearine is very old in the packing industry. The process has changed very little since its inception and is carried out as follows.

Crystallization of the fat, known in the industry as "graining" or "seed-ing," is carried out in small rectangular tanks, holding about 800 pounds each, which are mounted on trucks. After the tanks are filled with the melted fat, they are held for 3–4 days in a room maintained at 85–90°F., during which time the crystals are formed. As in other fractional crystallization procedures, it is essential that the crystals be formed slowly, in order that they will be large and easily separated from the un-crystallized oil.

After the desired degree of crystallization has taken place, the trucks are transferred to another room, where the oleo stock, now in the form of a thick, pasty, and grainy mass, is scooped from the trucks by hand, and wrapped, in portions of a few pounds each, in canvas press cloths. The latter are stacked in presses of the plate type, and subjected to moderate pressure, to yield oleo oil and residual cakes of oleostearine.

The fractional crystallization and pressing of lard, to yield edible lard oil, and of grease, for the production of inedible lard oil, is similar to that of oleo stock, except that it is carried out at a somewhat lower tempera-ture. i.e., at about 50°F.

5. Crystallization of Vegetable Stearines

Virtually the only commercial production of vegetable oil stearines is from coconut oil and other lauric acid oils, which are processed similarly to oleo oil or other animal fats, but at a lower temperature (about 72°F. for coconut oil), to yield a residue of the hard butter type, suitable for use as a confectioners' coating fat.

6. FRACTIONAL CRYSTALLIZATION OF FATTY ACIDS

(a) Production of Commercial Stearic and Oleic Acids by Conventional Method

The stock used in the preparation of commercial stearic acid and oleic acid (red oil) usually consists of relatively low-grade inedible tallow. After the fat is split (usually by the Twitchell process) and the resulting fatty acid distilled, the latter are charged into small shallow pans and caused to solidify by being slowly brought to a temperature of about 40°F. in a refrigerated room. The solid cakes produced by this operation are individually wrapped in press cloths and subjected to moderate pressure in a hydraulic plate press; the expressed liquid acids constitute commercial oleic acid or red oil. The latter is a rather impure product; in addition to oleic acid, it contains a considerable proportion of dissolved saturated acids, as well as most of the linoleic acid present in the tallow. Commercial products are said[11] ordinarily to contain between 60 and 70% of oleic acid. The titer is usually about 10°C., although rechilling, followed by filtration, is sometimes employed to reduce the titer to 2–5°C. Since saturated acids and linoleic acid may be present in approximately equal amounts, the iodine value is often close to that of pure oleic acid.

Cake from the cold pressing is melted, recast at room temperature, and again pressed in horizontal steam-heated presses. Pressing for a limited time produces the so-called single-pressed grade of stearic acid; more drastic pressing to expel additional liquid material yields "double-pressed" or "triple-pressed" acid. The press "foots" or expressed material is recycled to the feed stock, and in the manufacture of the higher grades the soft edges of the cakes are trimmed off and likewise recycled. Both stearic acid and red oil are usually bleached rather heavily with acid-activated earth and carbon before they are marketed.

The production of commercial stearic and oleic acids, like other fractional crystallization operations mentioned above, depends upon the formation of large and well-formed crystals from which liquid material may be readily expressed. It is fortunate that in tallow the relative proportions of palmitic and stearic acids (about 55 parts to 45)[12] are such that good crystals are deposited from the mixture. Because of the poor crystallinity of mixtures substantially higher or lower in stearic acid, the method is not applicable to the mixed acids from most other fats.[13]

[11] D. Swern, H. B. Knight, and T. W. Findley, Oil & Soap, 21, 133–139 (1944).
[12] B. Nicolet, J. Ind. Eng. Chem., 12, 677–679 (1920).
[13] R. L. Demmerle, Ind. Eng. Chem., 39, 126–131 (1947).

(b) Fractional Crystallization of Fatty Acids from Solvents

The recently introduced Emersol process[8,13,14] produces red oil and stearic acid equivalent to the best double- or triple-pressed grades by the continuous fractional crystallization of tallow fatty acids from 90% methyl alcohol. One of the larger American fatty acid plants now uses the process exclusively.

Crystallization is carried out by pumping the fatty acid–solvent mixture through cooled cylinders equipped with slow-moving internal scraper blades, and filtration is effected on an enclosed drum type filter equipped with a string cake discharge. The solvent was selected on the basis of its cost, stability, volatility, and low dissolving power for saturated acids, and also its characteristic of depositing fatty acid crystals in the form of needles that are easily filtered and washed. Petroleum naphthas and chlorinated solvents were found to produce crystals of a less desirable platelike form.

In addition to its economy, and the good quality of the products, the process is outstanding for its versatility, i.e., its ability to effect separations of solid and liquid acids in proportions that are impossible to handle by the older pressing method.

Because of its improved flexibility, its markedly superior operating economy, and the greater purity of its products, the solvent crystallization process may be expected to assume increasing importance in the fatty acid industry. At the present time (1950) there are under construction or in operation at least three American plants which will process fatty acids with solvents other than methyl alcohol. One manufacturer has announced[15] a new line of very pure "stearic" acids, produced by an undisclosed solvent process, which are made to the remarkable specifications of a maximum iodine value of 0.5 and a maximum content of unsaponifiable matter of 0.2%. The forthcoming commercial production of pure oleic and linoleic acids by solvent crystallization has been announced by another producer.[15a]

C. Liquid-Liquid Extraction

The liquid-liquid extraction process for the fractionation of fatty acids and glycerides or other fatty acid esters is dependent upon the fact that, ordinarily, liquid fatty materials become increasingly soluble in organic solvents as they become more unsaturated or as their molecular weight decreases. Thus, if a mixture of fatty compounds is brought to

[14] L. D. Myers and V. J. Muckerheide (to Emery Industries), U. S. Pats. 2,293,676 (1942) and 2,298,501 (1942).
[15] See *Chem. & Eng. News*, *27*, 3592 (1949).
[15a] See *Chem. & Eng. News*, *28*, 292 (1950).

equilibrium in contact with a solvent with which it is incompletely miscible and the two phases are allowed to separate, the portion of fat dissolved in the solvent phase will be different in composition from that remaining in the fat phase. An experiment cited by Freeman[16] will illustrate this effect: One part by volume of soybean oil with an iodine value of 136 was agitated with four parts of furfural at a temperature of 27°C., and the two were allowed to separate. By distilling the furfural from each fraction, there was obtained 28% of an extract with an iodine value of 146, and 72% of residual oil or raffinate with an iodine value of 132.
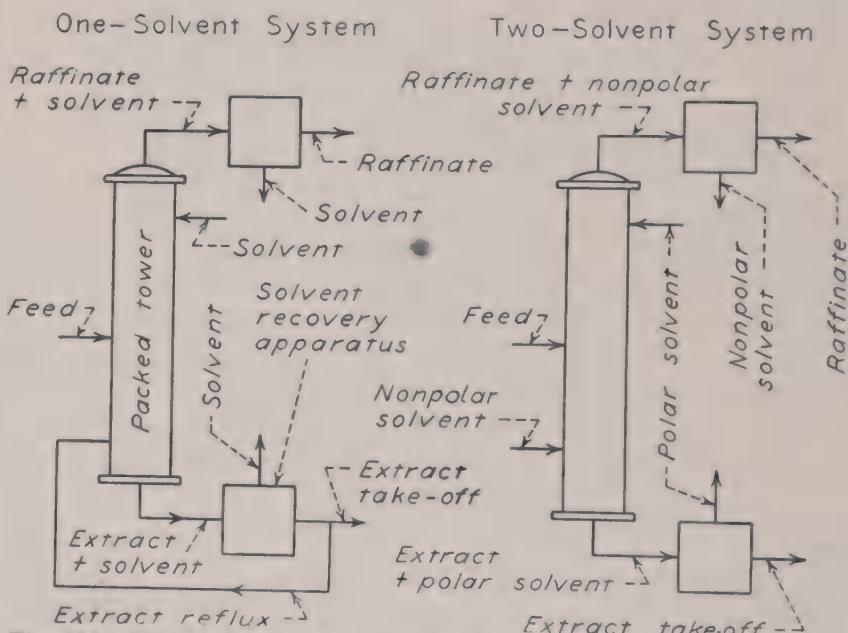
Fig. 154. Simplified flow diagrams for liquid–liquid extraction with furfural, single and dual solvent systems.

In practice, liquid-liquid extraction is carried out continuously in tall columns in which the solvent and the fat come into contact in countercurrent flow; the fat is fed into the column at a point intermediate between the bottom and top, and only a portion of the extract issuing from the column is taken off, the remainder being freed of solvent and returned to the column as reflux, to increase the efficiency of separation. As an alternative to the return of extract, a second solvent, miscible with the oil, but immiscible with the first solvent, may be fed into the column to provide reflux. Schematic diagrams of the two systems, employing a heavy polar solvent immiscible with the fat and a miscible nonpolar solvent, are shown in Figure 154. For descriptions

[16] S. E. Freeman (to Pittsburgh Plate Glass Co.), U. S. Pat. 2,200,391 (1940).

of the many possible variations of the process, including the use of multiple columns and combination reflux systems, reference should be made to the publications of Gloyer[17] and Passino.[18]

Since the extraction rate in liquid-liquid extraction is controlled by a process of molecular diffusion between adjacent layers of two immiscible liquids, the methods employed in calculations of absorption, distillation, or other diffusion processes, are likewise applicable to calculations for the design of extraction towers. A general review of methods for design calculations in liquid-liquid extraction has been presented by Elgin.[19]

It has been repeatedly pointed out[20] that the principles applicable to fractional distillation all have their counterpart in liquid-liquid extraction. Just as an appreciable difference in the vapor pressures of two components will permit their separation by distillation (the completeness of separation depending upon the size of the fractionating column and the capacity at which it is operated), so will a difference in the affinity of two components for a solvent permit their separation by liquid-liquid exartction. In the case of fats and oils, the attainable degree of separation is limited by the mixed nature of the glycerides. However, the degree to which the separation of fatty acids or their monoesters may be carried is defined principally by economic considerations relating to the size of the extraction towers and the practicable limits to which refluxing may be carried.

1. SOLVENTS FOR LIQUID-LIQUID EXTRACTION

The solvents which are sufficiently immiscible with fatty materials at ordinary temperatures and pressures to be effective for liquid-liquid extraction are all highly polar compounds. Different compounds differ considerably in their effectiveness according to the number of polar groups in relation to the size of the molecule, and also their position in the molecule. According to the rule stated by Freeman,[16] for a solvent to be effective it must contain at least one polar group to each 4 to 6 carbon atoms in the molecule, and in the case of the weaker polar groups this ratio must be somewhat increased. The permissible number of carbon atoms for each of several groups is listed in Table 131.

Among the polar solvents which have been reported to be effective in liquid-liquid extraction are the following: nitroethane, methyl cellosolve, methyl formate, methyl levulinate, furfural, propionitrile, trimethyl phosphate, actaldehyde, triethyl phosphate, acetonyl acetone,

[17] S. W. Gloyer, *Ind. Eng. Chem.*, *40*, 228–236 (1948).
[18] H. J. Passino, *Ind. Eng. Chem.*, *41*, 280–287 (1949).
[19] J. C. Elgin, *Chem. & Met. Eng.*, *49*, No. 5, 110–116 (1942).
[20] See, for example, T. G. Hunter and A. W. Nash, *J. Soc. Chem. Ind.*, *53*, 95–102T (1934); E. W. Thiele, *Ind. Eng. Chem.*, *27*, 392–396 (1935); W. H. Goss, *J. Am. Oil Chem. Soc.*, *26*, 584–588 (1949).

diacetyl, nitromethane, glycol diacetate, ethyl oxalate, methyl cellosolve acetate, methyl lactate, ethyl lactate, cellosolve, ethyl maleate, acetic anhydride, carbitol, etc. However, furfural appears to combine selective action toward unsaturated acids with other desirable characteristics to an optimum extent, and apparently is the only polar solvent which has been used to any extent in practice. Furfural is miscible with fatty acids and their monoesters at ordinary temperatures, but is completely miscible with glycerides only at a somewhat elevated temperature. Hence, on the acids and monoesters it can be used only in connection with a nonpolar solvent. In the fractionation of oils, furfural can be used either alone or as one component of a two-solvent system, according to the temperature chosen for operation. A suitable and cheap nonpolar solvent is ordinary petroleum naphtha.

Among the basic patents applying to the liquid-liquid extraction of fatty materials with furfural and similar solvents are those of Freeman, Batchelder, Goss and Johnstone, and Jenkins.[21]

TABLE 131

PERMISSIBLE NUMBER OF CARBON ATOMS FOR SOLVENT EFFECTIVENESS

Polar group	Number of C atoms per group	Polar group	Number of C atoms per group
—PO₄	6	—NO₂	2
—C=O \ O \ —C=O	4	CO₃	2
		NH₂	2
		SO₄	>2
—OH	3	NH	1
—CO	3	—O—	1
—COO—	3	—S—	1
—CN	3	N—	1
—CHO	2		
—COOH	2	C=C	1

[21] See the following: S. E. Freeman (to Pittsburgh Plate Glass Co.), U. S. Pats. 2,200,390-1 (1940); 2,278,309 and 2,291,461 (1942); 2,313,636 and 2,316,512 (1943). A. H. Batchelder (to Standard Oil Co. of Calif.), U. S. Pat. 2,285,795 (1942). W. H. Goss and H. F. Johnstone (to Secretary of Agriculture), U. S. Pat. 2,290,609 (1942). J. D. Jenkins (to Pittsburgh Plate Glass Co.), U. S. Pat. 2,320,738 (1943).

In the so-called Solexol process[18,22–24] the solvent is liquid propane, which near its critical temperature (*ca.* 206°F. or 97°C.) undergoes a large decrease in density and becomes incompletely miscible with fats. The action of liquid propane on fats is the reverse of that of furfural, etc., in that the saturated rather than the unsaturated components are preferentially dissolved by the solvent. (However, in liquid propane, as in polar solvents, the solubility of fats increases with decrease in the molecular weight.[22,24a]) Furthermore, liquid propane is unlike furfural, lighter than fat or fatty acids, hence the extract is taken off the top of the column, whereas a furfural column discharges the extract at the bottom. When used for fractionation, propane columns are commonly operated with an appreciable temperature gradient from top to bottom. By maintaining progressively lower temperatures as the bottom is approached, there is created, in effect, a series of solvents of varying dissolving power up and down the column. This has the effect of producing a certain amount of internal reflux, which supplements the reflux obtained by the conventional method.[18]

2. LIQUID-LIQUID EXTRACTION IN PRACTICE

The design and operation of commercial and semicommercial furfural columns for soybean and linseed oil have been described by Gloyer[17] and by Kenyon *et al.*[25] A column 5.5 feet in diameter, with 67 feet of Raschig ring packing, operating at an oil feed rate of 500 gallons per hour, with a 6 to 1 solvent ratio, and refluxing 4 parts of extract for each 1.0 part taken off, fractionates linseed oil of 180.1 iodine value into a 25% raffinate fraction of 132.2 iodine value and a 75% extract fraction of 196.3 iodine value. A greater spread in iodine value between raffinate and extract is obtainable, at reduced capacity, by operating at a greater solvent ratio (up to 14 to 1), with more reflux, or with a greater column height. With soybean oil, laboratory studies indicated that maximum fractionation would be accomplished in a column with 72 feet of packing with a solvent ratio (solvent to oil) of 14 to 1 and a reflux ratio (extract refluxed to extract taken off) of 4.0 to 1. With 87 feet of packing the corresponding ratios were 10 to 1 and 2.6 to 1, respectively; and with 95 feet, they were 8 to 1 and 1.8 to 1. The use of a second solvent (petroleum naphtha) for supplementary reflux is markedly advantageous in dealing with unrefined or undegummed oil containing phosphatides

[22] A. W. Hixson and J. B. Bockelmann, *Trans. Am. Inst. Chem. Engrs.*, *38*, 891–930 (1942).
[23] D. A. Drew and A. N. Hixson, *Trans. Am. Inst. Chem. Engrs.*, *40*, 675–694 (1944).
[24] A. W. Hixson and R. Miller (to Chemical Foundation), U. S. Pat. 2,219,652 (1940).
[24a] R. Bogash and A. N. Hixson, *Chem. Eng. Progress*, *45*, 597–601 (1949).
[25] R. L. Kenyon, S. W. Gloyer, and C. C. Georgian, *Ind. Eng. Chem.*, *40*, 1162–1170 (1948).

and other impurities, as these impurities may thereby be separated from the extract in a small cut taken off the bottom of a second column. Column temperatures are in the range of 80–125°F., depending upon the oil being fractionated and other operating conditions. The original article of Kenyon *et al.*[25] gives extensive data on the design of the solvent recovery system. For further data on the composition of the extraction products, see Chapter XII.

Operating data on the liquid propane process for fractionating fats have not been published, although some information is available on a plant used for the refining (decolorization) of inedible tallow.[26] It appears that throughput rates, solvent ratios, reflux ratios, column heights, etc., are probably not markedly different from those employed in furfural extraction. From published data on the phase characteristics of propane–fat systems,[22] the useful working range for fats (glycerides) would appear to be from about 150° to 180°F. (65–82°C.), which corresponds to pressures of the order of 350–500 pounds. Because of the rapidity with which the solubility of the fat changes as the temperature of the solvent is raised (tallow, for example, is completely soluble at about 150°F. and almost completely insoluble at 180°F.), temperature control is very much more critical than in the furfural process. With respect to the unsaturation of fatty materials, propane is claimed to be inherently less selective than furfural.[27]

Liquid-liquid extraction experiments with solvents other than furfural and propane have apparently been confined to the laboratory. The one instance of reported work on the fractionation of a fat with respect to molecular weight of the glycerides,[28] was carried out on coconut oil with 95% ethyl alcohol as the solvent. Liquid-liquid extraction with alcohol has been suggested as a means of fractionating mixtures of mono-, di-, and triglycerides.[29]

Behr[30] achieves a segregation of the highly unsaturated, polymerizable glycerides of fish oils by polymerizing the oils, and extracting the polymerized oils with ketones or higher alcohols to remove the relatively saturated, unpolymerized portions. A similar treatment is applied to linseed oil to produce the so-called Tekaols.[31]

Liquid-liquid extraction after saponification is employed for the recovery from oils of sterols, vitamin A, or other unsaponifiable con-

[25] E. B. Moore, *J. Am. Oil Chem. Soc.*, **27**, 75–80 (1950).
[27] W. H. Goss, *J. Am. Oil Chem. Soc.*, **26**, 584–588 (1949).
[28] W. R. Fish, M. H. Menaker, P. M. Althouse, and H. O. Triebold, *Oil & Soap*, **22**, 317–319 (1945).
[29] R. O. Feuge and A. T. Gros, *J. Am. Oil Chem. Soc.*, **27**, 117–122 (1950).
[30] O. M. Behr (to Vegetable Oil Products Co.), U. S. Pat. 2,239,692 (1941). See also W. H. Mattil, *Oil & Soap*, **21**, 197–201 (1944).
[31] E. Rossmann, *Angew. Chem.*, **50**, 246–248 (1937).

stituents. In this application it is usually carried out batchwise, in multiple stages.

D. Distillation

1. THEORY AND GENERAL PRACTICE

The vapor pressures of triglycerides are generally too low to permit them to be distilled without decomposition except by the technique of molecular distillation. On the other hand fatty acids and their mono-esters may be readily distilled at pressures of the order of 1–5 mm. and temperatures of the order of 400–450° (200–235°C.), and monoglyc-
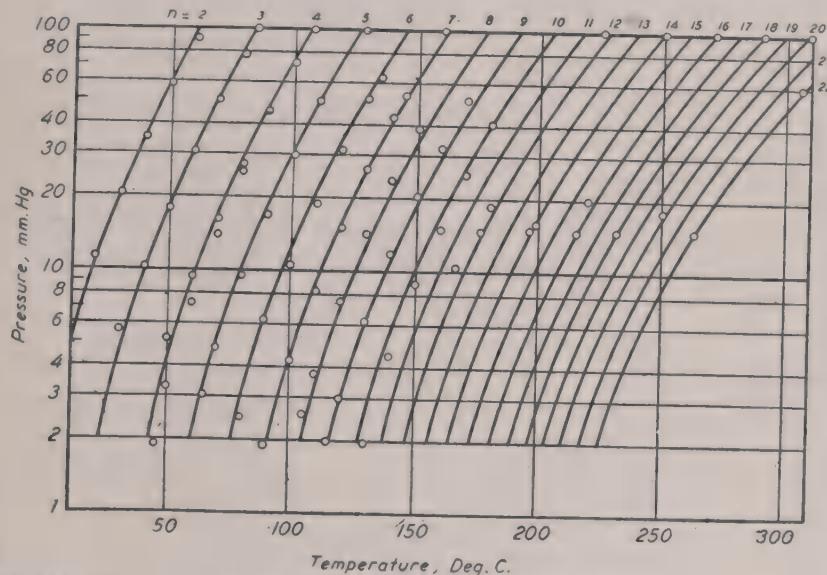
Fig. 155. Vapor pressures of fatty acids (n = number of C atoms in acid).[32]

erides may be fractionally distilled from mixtures containing di- and triglycerides.[31a]

Whereas fractional crystallization and liquid-liquid extraction effect a fractionation of fatty materials upon the basis of their relative degree of unsaturation, the fractionation produced by distillation is almost en-tirely according to molecular weight or chain length. Fatty acids or esters of a given chain length exhibit but very slight differences in vola-tility with different degrees of unsaturation. It is a matter of difficulty, for example, to produce a separation of oleic and stearic acids by distilla-tion even in the most efficient laboratory columns, and commercially such a separation does not appear practicable. On the other hand, there is

[31a] J. Ross, A. C. Bell, C. J. Arrowsmith, and A. I. Gebhart, *Oil & Soap*, *23*, 257–259 (1946).

a marked difference in the volatility of any two fatty acids of different chain length. In the range of temperatures within which distillation is practicable, the vapor pressure of a fatty acid at a fixed temperature is more than doubled for each decrement in chain length of two carbon atoms (see Fig. 155[32]).

By working carefully with an efficent laboratory column, Norris and Terry[33] found it possible to separate methyl stearate and methyl oleate by distillation. However, they could not separate methyl oleate and methyl linoleate, even though the difference in boiling point (ca. 3°C.) was equal to that between the stearate and the oleate. The difficulty in the latter case was attributed to extensive molecular association of the two compounds. Terry and Wheeler[34] have reported that the methyl esters of conjugated and nonconjugated octadecadienoic acids produced by alkali isomerization can be separated in the laboratory by fractional distillation.

While fractionation of a fatty acid mixture by distillation cannot be accomplished upon the basis of differences in unsaturation alone, it so happens that in many cases distillation of the mixed acids from an oil will yield fractions differing greatly in iodine value, due to the particular composition of the oil. Thus, for example, the saturated acids of cottonseed oil, soybean oil, and many other vegetable oils consist preponderantly of palmitic acid, a C_{16} acid. Separation of C_{16} and lower acids from the mixed fatty acids of these oils will leave a residue consisting largely of oleic and linoleic acids, and hence considerably more unsaturated than the original oil. Soybean oil fatty acids so fractionated are porduced commercially with an average iodine value of 147.5, whereas the average iodine value of the original acids is about 136.

Fish oils may be fractionated to an even greater extent, inasmuch as their highly unsaturated fatty acids contain 20 and 22 carbon atoms and hence are easily separable from the less unsaturated C_{14}, C_{16}, and C_{18} acids. Mixed sardine oil fatty acids (with an iodine value of about 195) are commercially distilled to produce a fraction with an iodine value as high as 250.[35]

From coconut oil fatty acids or other fatty acid mixtures comprising a variety of saturated acids of different chain length it is easily possible to prepare by distillation fractions consisting substantially of single fatty acids. Thus caprylic, capric, lauric, myristic, palmitic, and stearic acids have all been prepared commercially with purities of 90% or better. It is to be noted that fractionally distilled stearic acid is some-

[32] Attributed by E. Schlenker to W. Gensecke. See H. Schönfeld, ed., *Chemie un Technologie der Fette und Fettprodukte*, Vol. II, Springer, Vienna, 1937, p. 508.
[33] F. A. Norris and D. E. Terry, *Oil & Soap*, 22, 41–46 (1945).
[34] D. E. Terry and D. H. Wheeler, *Oil & Soap*, 23, 88–90 (1946).
[35] D. V. Stingley, *Ind. Eng. Chem.*, 32, 1217–1220 (1940).

what different from ordinary commercial "stearic acid," which actually is a mixture of stearic acid with an equal or greater proportion of palmitic acid.

In a number of processes, some of which have been used commercially, distillation of fatty acids or monoesters is preceded by treatment to cause polymerization of some relatively unsaturated component and thus reduce its volatility. A technique highly effective in separating polymerizable from relatively saturated and hence nonpolymerizable fractions of fatty acids or monoesters consists of heat treating the mixed acids or esters to the point of dimerization of the reactive members, and separating the resulting monomers and dimers by fractional distillation.[36] Goebel[37] has reported that a modification of this technique is effective for the dimerization and separation as dibasic acid of the linoleic acid present in commercial oleic acid; in the presence of 1–5% moisture, dimerization occurs without extensive decomposition or decarboxylation at 330–370°C. (626–698°F.). The patent of Carleton[38] contemplates selective splitting of unpolymerized and relatively saturated glycerides during the heat bodying of drying oils, followed by distillation of the fatty acids. The patent of Barnitz[39] covers the molecular distillation of unpolymerized glycerides from bodied oils.

2. Purification of Fatty Acids by Distillation

Since commercial fatty acids are commonly derived from the lowest grades of fats, including very dark tallows and greases, and foots remaining from the refining of vegetable oils, they require purification. Purification of the crude fatty acids is effected by distillation, which not only accomplishes the removal of pigments and other relatively nonvolatile impurities, but also separates the acids from any residue of unhydrolyzed oil remaining from the splitting operation.

Fatty acid distillation is invariably carried out under reduced pressure, and usually with the aid of stripping steam, at temperatures in the range of about 400–450°F. (204–232°C.). The maximum permissible temperature depends principally upon the possibility of polymerizing the acids to an excessive degree. A highly unsaturated stock cannot be distilled at as high a temperature as a stock of low iodine value, and if the distillation equipment is so designed as to require the stock to be kept hot for a long period it cannot be operated at as high a temperature as equipment in which the acids are heated and distilled more

[36] See T. F. Bradley and W. B. Johnston, *Ind. Eng. Chem.*, *32*, 802–809 (1940); T. F. Bradley (to American Cyanamid Co.), U. S. Pat. 2,350,583 (1945).
[37] C. G. Goebel, *J. Am. Oil Chem. Soc.*, *24*, 65–68 (1947).
[38] R. A. Carleton, U. S. Pat. 2,367,666 (1945).
[39] E. S. Barnitz (to Distillation Products, Inc.), U. S. Pat. 2,437,343 (1948).

quickly. Low molecular weight acids are naturally distilled at lower temperatures than acids of high molecular weight.

At high temperatures fatty acids are very corrosive to ordinary carbon steel. The most suitable material for the construction of stills is Inconel or Type 316 or other stabilized stainless steel. Ordinary Type 304 stainless steel is said to be not much more resistant than ordinary steel.

Formerly the most common type of fatty acid still consisted simply of a direct-fired pot equipped with a source of superheated steam, condensers, and some sort of vacuum pump. Recent installations, however, have consisted very largely of continuous stills. The latter offer a number of advantages over batch stills, including an improved yield of distilled acids. In continuous distillation the time that the fatty acids are in the apparatus is much reduced, and there is consequently less loss from polymerization. The residue of unsplit fat and polymerized fatty acids, known as still or stearine pitch, is used in floor tiling, electrical insulation, industrial paints, etc. In batch stills operating on some stocks it may represent a substantial part, *e.g.*, 10% or more, of the total product.

One of the earliest and most successful forms of continuous fatty acid stills was devised by Wecker.[40] In the Wecker system, vaporization of the acids is effected in a closed, flat, rectangular, traylike chamber, divided internally into compartments, and heated from beneath by a large number of gas burners. The feed stock, preheated in a heat exchanger with steam, flows horizontally through the compartments of the chamber in series. It is either stripped or partially stripped of fatty acids during its passage through the chamber, and discharges from the end of the chamber remote from the intake as stearine pitch, or incompletely distilled stock, the residue passing successively to a cooler, a receiving tank, and a discharge pump.

The stripping medium, which is injected into each of the compartments within the vaporization chamber, consists of wet steam, produced by bringing together streams of superheated steam and cold water. According to the Wecker patent claims, water may alternatively be atomized into nitrogen or other inert gas. The use of a fog of water, rather than saturated or superheated steam, apparently leads to more violent agitation and increased stripping efficiency in the stripping tray.

In the Wecker still, as in other acid stills, the vapor stream of mixed fatty acids and steam is first partially cooled, to condense and remove the fatty acids, and then further cooled, to condense the steam. The vapor pressures of water and fatty acids are sufficiently different that there is no difficulty in selectively condensing the two, although there is some tendency for the steam to carry a fog of liquefied acids, after the latter have been condensed. Various devices are employed to assist in

[40] E. Wecker, Ger. Pat. 397,332; Brit. Pat. 213,267 (1923); U. S. Pat. 1,622,126 (1927).

the mechanical separation of the steam and the entrained acids. The separated acids discharge to a receiving tank from which they are continuously pumped out of the system. Vacuum is maintained on the system by a positive displacement pump placed beyond the steam condenser.

The vacuum obtained in the Wecker apparatus depends upon the temperature and vapor pressure of the condenser water, hence the absolute pressure will not usually be lower than about 15 to 30 mm. The time required for the material to pass through the apparatus is said ordinarily to be 10 to 15 minutes. This system is not adaptable to close fractionation of fatty acid mixtures, although some degree of fractionation may be obtained by using different units in series, or by passing material repeatedly through the same unit at successively increasing temperatures. It is suitable for the steam refining of oils.

Many late installations of fatty acid stills in the United States have employed ordinary tray and bubble cap towers, with the feed stock and the stripping steam being heated by Dowtherm vapor.[41] Dowtherm heating is highly advantageous in comparison with direct firing, as Dowtherm vapors can be condensed at a temperature only slightly above that desired in the feed stock, and thus overheating and polymerization of acids in stagnant films or "dead spots" is entirely avoided.

Complete equations for the calculation of problems in both batch and continuous steam distillations have been given by Garber and Lerman.[42]

The Mills[43] continuous fatty acid distillation process avoids the use of stripping steam by preheating the feed stock to 550–575°F. in a Dowtherm heater, passing the heated material into a still maintained under a pressure of about 2 mm. of mercury to flash off 75–80%, reheating the bottoms from the still to 575–590°F., and again flashing in a second still with vapor passages interconnected with the first, to increase the recovery of fatty acids to about 95% of the feed. The preceding temperatures apply to once-through operation of the system. By recycling 34% of the primary feed and 69% of the secondary feed sufficient heat can be applied to the stock to induce vaporization without the temperature of either feed being above 515°, even at a pressure of 4 mm.

A special feature of the Mills still is a central draft tube into which the incoming mixture of liquid and vapors from the preheaters discharges, inducing an upward flow of liquid from the still bottom against a baffle placed over the top of the tube. This produces an umbrella-shaped curtain of liquid between the flashing vapors and the vapor outlet, which serves as an effective entrainment separator. An essential feature of the process is throttling of the liquid streams on the inlet rather than the

[41] For a flowsheet of a typical plant, see *Chem. Eng.*, *55*, No. 2, 146–149 (1948).
[42] H. J. Garber and F. Lerman, *Trans, Am. Inst. Chem. Engrs.*, *39*, 113–131 (1943).
[43] V. Mills (to Procter & Gamble Co.), U. S. Pats. 2,274,801–2 (1942).
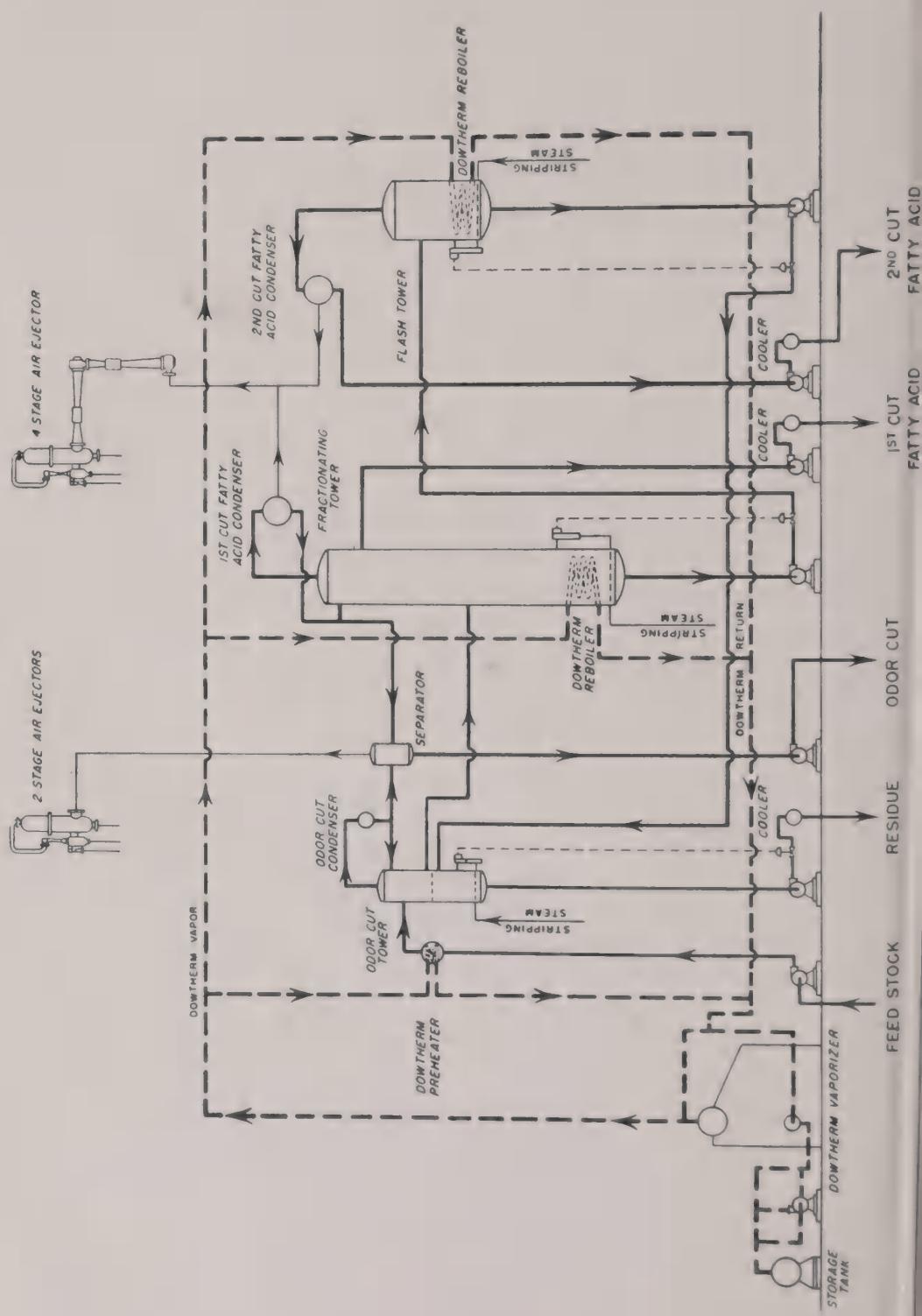
discharge side of the preheaters. It was designed primarily for the distillation of fatty acids prior to saponification in continuous soapmaking, and presumably is not used for distilling highly unsaturated acids.

Although distillation of the fatty acids from a low-grade fat will remove most of the impurities, the presence of minor amounts of color bodies, unsaponifiable matter, etc., in the distillate is still a matter of some concern to the fatty acid distiller. Methods for minimizing the distillation of impurities are the subject of patents by Sheely,[44] McKee and Graziani,[45] and McClain[46] (Section C-3, Chapter XVI).

3. Fractional Distillation of Fatty Acids

The essential features of a modern plant[47] for the fractional distillation of fatty acids are shown in Figure 156 (see also Fig. 157). The Dowtherm preheated feed stock is first put through a small fractionating tower to take off a small overhead fraction high in odoriferous material and color bodies. Part of the distillate from the overhead condenser is returned to the tower as reflux and the remainder is withdrawn. Moderate vacuum is maintained on the tower by means of a two-stage steam ejector with barometric intercondenser.

A liquid side stream consisting of most of the original feed passes to the main fractionating tower, which is maintained under a pressure of 2 mm. by a four-stage steam ejector system, and provided with a Dowtherm-heated reboiler which supplies heat for operation of the column. The overhead distillate from the main tower, containing the remainder of the odor and color-bearing constituents, is partially returned to the tower as reflux and partially combined with the odor cut taken off the first tower. The first fatty acid cut, consisting of the lower boiling fatty acids in the feed stock, e.g., palmitic in a mixture of palmitic and stearic, is taken off as a liquid side stream near the top of the tower.

Bottoms from the main tower are pumped to a third "flash tower," which is likewise equipped with a Dowtherm-heated reboiler and maintained under 2 mm. pressure. The overhead from this tower is taken off as the second fatty acid cut (of higher boiling acids). Bottoms from the tower are pumped to a stripping tower (actually the bottom section of the first tower), and, after steam stripping to remove residual volatile fatty acids, are taken off as stearine pitch. The second and third tower

[44] M. L. Sheely (to Armour & Co.), U. S. Pat. 2,062,837 (1936).
[45] J. E. McKee and O. Graziani (to Armour & Co.), U. S. Pat. 2,304,842 (1942).
[46] H. K. McClain (to Procter & Gamble Co.), U. S. Pat. 2,435,456 (1948).
[47] R. L. Kenyon, D. V. Stingley, and H. P. Young, Ind. Eng. Chem., 42, 202–213 (1950).

condensers are cooled with liquid Dowtherm circulated in a closed system and cooled in a tubular heat exchanger.

4. MOLECULAR DISTILLATION

Large-scale molecular distillation[48] is principally useful for producing vitamin A concentrates from fish liver oils and vitamin E (tocopherol)
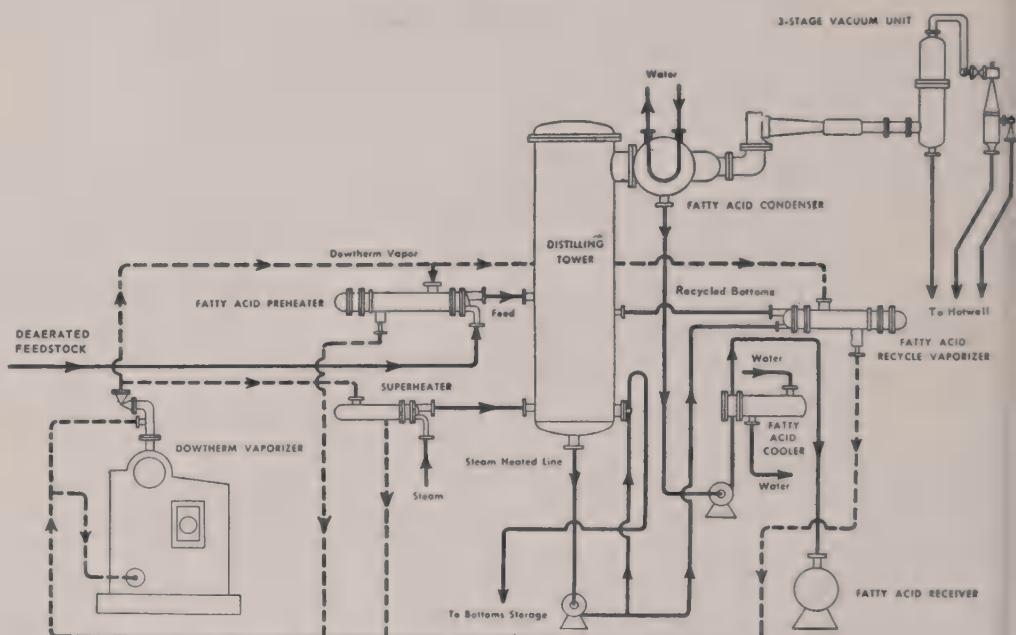
Fig. 157. Simplified flow diagram for continuous distillation of fatty acids without fractionation. (Courtesy of *The Foster Wheeler Corp.*).

concentrates from vegetable oils, although other nonglyceride substances of possible commercial value, including sterols[49] and hydrocarbons[50] can also be separated from oils by this method of distillation, and recently molecular distillation has been used on a commercial scale[51,52] to produce monoglycerides of high purity (above 90%) from the equilibrium mixtures of mono-, di-, and triglycerides resulting from the reaction of fats with an excess of glycerol. The use of molecular distillation for

[48] For recent articles on commercial molecular distillation, see K. C. D. Hickman, *Chem. Revs.*, *34*, 51–106 (1944) and *Ind. Eng. Chem.*, *39*, 686–694 (1947); T. R. Olive, *Chem. & Met. Eng.*, *51*, No. 8, 100–104 (1944).

[49] K. C. D. Hickman, *Ind. Eng. Chem.*, *32*, 1451–1453 (1940).

[50] J. G. Baxter (to Distillation Products, Inc.), U. S. Pat. 2,169,192 (1939).

[51] N. H. Kuhrt, E. A. Welch, and F. J. Kovarik, *J. Am. Oil Chem. Soc.*, *27*, 310–313 (1950).

[52] N. H. Kuhrt and E. A. Welch, *J. Am. Oil Chem. Soc.*, *27*, 344–346 (1950).

separating monomers from dimers and other polymers in heat-bodied oils has been suggested.[39]

The conditions required for efficient molecular distillation on a laboratory scale must be duplicated in commercial distillation. In other words, a thin and uniform film of the thoroughly degassed, hot, and turbulently moving oil must be continuously passed in proximity to a relatively cold condensing surface, and the space between the oil film and the condenser must be maintained at a vacuum of the order of 0.001 mm., or about one-millionth of an atmosphere, in order to permit free passage of molecules of the distillate between the two surfaces.[53]
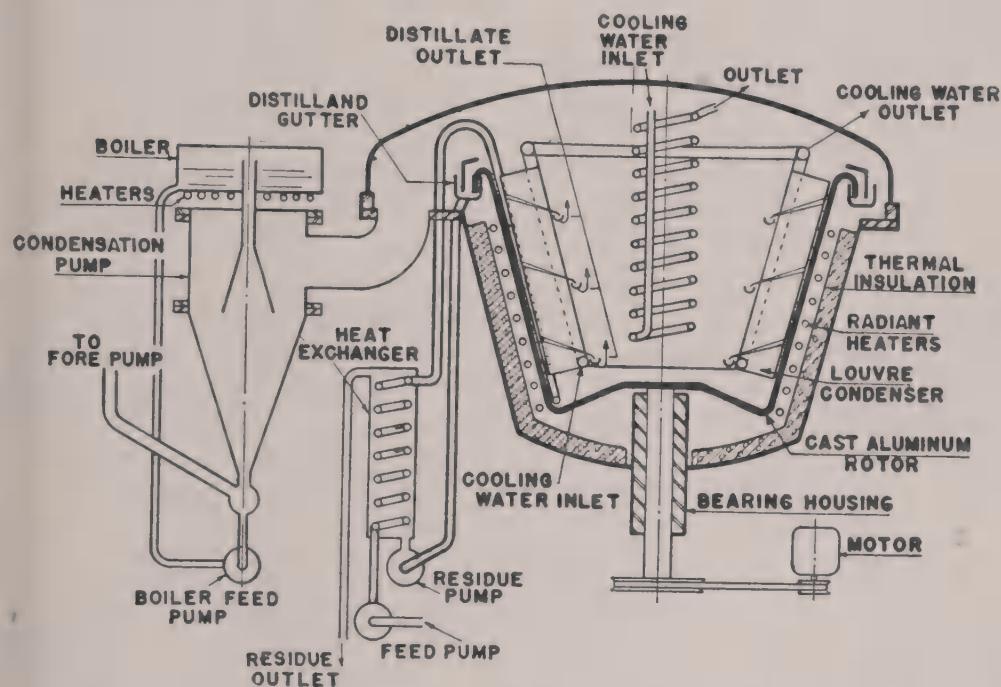
Fig. 158. Diagrammatic view in elevation of a commercial centrifugal molecular still.[55]

The design of equipment capable of fulfilling the above conditions, and of presenting large evaporating and condensing surfaces within a reasonably compact apparatus, presents considerable difficulty. An ordinary laboratory still of the falling-film type translated to large dimensions is extremely lacking in compactness, and in addition, films moving under the force of gravity are insufficiently thin and insufficiently turbulent to provide the most rapid and efficient distillation. The molecular stills de-

[53] For treatment of the theory of molecular distillation, see K. C. D. Hickman, *Chem. Revs.*, *34*, 51–106 (1944); also R. S. Bradley and A. D. Shellard, *Trans. Faraday Soc.*, *45*, 501–507 (1949).

signed by Hickman[54,55] overcome these difficulties by employing rapidly revolving members for spreading the oil by centrifugal force. A commercial still with a 5-foot rotor is shown in diagrammatic elevation in Figure 158. The rotor, of polished aluminum, has the form of a "flower pot" with sides inclined 10–25° from the vertical which turns at 400 r.p.m. inside a gastight housing exhausted by means of suitable vacuum pumps. It is heated by radiant electrical resistance heaters mounted in the form of a nest between the rotor and the housing. The feed oil, partially preheated and degassed, is fed into the bottom of the rotor, near the periphery; under the influence of centrifugal force it flows in a thin (ca. 0.05 mm.), uniformly distributed, and turbulent film up the inside of the rotor, and discharges from the upper rim of the rotor into a gutter from which it is continuously removed by a distilland or residue pump. Material evaporating from the oil film is condensed upon the cooled surfaces of a vertical leaf condenser adjacent to the inner surface of the rotor and is taken off from gutters placed at three levels in the condenser assembly. By maintaining the surfaces supplying the various gutters at different temperature levels, it is possible to separate the total distillate into three fractions varying in distillability. Vacuum is maintained on the unit by a large condensation pump backed by five-stage steam ejectors. The unit is operated at feed rates varying from 50 to 250 gallons per hour. Oil fed at the rate of 750 kg. (1650 pounds) per hour, at a temperature of 200°C. (392°F.), remains on the rotor 1.2 seconds.

The molecular still is particularly well adapted to handling heat-labile materials, as the latter need be heated only during the very short period that it is on the rotor, and the temperatures required are, of course, much lower than for conventional distillation. Its greatest disadvantage is that the principle of rectification employed in conventional distillation is inherently inadaptable to it, and hence the possible degree of separation of components of varying volatility is limited. However, where it is desired to separate a light or heavy component from other components present in great excess, separation can be improved by multiple redistillation, in separate stills or, by modification of the apparatus within the same still.[56] Hickman[55] has pointed out that, in any case, the separation achieved in a single distillation is commonly two to three

[54] Various forms of centrifugal stills, all embodying the same basic principle, are described in U. S. Pats. 2,210,927–8; 2,218,240; 2,234,166; 2,249,526; and 2,298,377, all issued to K. C. D. Hickman and assigned to Distillation Products, Inc.

[55] K. C. D. Hickman. Ind. Eng. Chem., 39, 686–694 (1947).

[56] See Hickman, footnote 55, and also E. W. Fawcett and J. L. McCowen (to Imperial Chemical Industries Ltd.), U. S. Pat. 2,073,202 (1937) and R. G. J. Fraser (to Imperial Chemical Industries Ltd.), U. S. Pat. 2,128,223 (1938). See also the description of a multi-stage apparatus in Chem. Eng., 57, No. 8, 131 (1950) and J. Research Natl. Bur. Standards, 44, 135 (1950).

times as efficient as that in a conventional unstirred pot still operating under high vacuum.

E. Other Separation Methods

1. Methods Involving Chemical Reaction

In a few instances, methods have been proposed or used for the commercial separation of fatty materials which involve a prior chemical reaction of the fat other than polymerization. A standard laboratory technique for isolating saturated fatty acids or glycerides includes an oxidation step in which the unsaturated components of the mixture are converted to water-soluble compounds of low molecular weight.[57,58] The method of Fitzpatrick and Myers[59] for removing unsaturated fatty acid impurities from saturated fatty acids is similar. It involves treatment of the crude saturated acids with chromic acid and removal of low molecular weight acids by distillation and water extraction.

Dunlap and co-workers[59a] have described an esterification technique for separation of the fatty acids from the rosin acids in tall oil. According to their data, reaction of tall oil with glycerol at 180°C. for six hours results in virtually complete esterification of the fatty acids, without appreciable reaction of the rosin acids.

A method has been proposed[60] for separating saturated and unsaturated fatty acids which is based upon the preference for alkalies forming soluble soaps to react with unsaturated acids and of alkalies forming insoluble soaps to react with saturated acids. According to the patent of Sanders,[60a] saturated fatty acid may be liberated preferentially to relatively unsaturated fatty acids in fish oils by treating the oils with lipolytic enzymes. Actually, in this case, however, selective hydrolysis depends upon the chain length of the acids, rather than their unsaturation. The preferential neutralization of fatty acids with mixed alkalies has recently been reinvestigated by Nicholsen and Formo,[61] who found, for example, that by treating soybean oil fatty acids (iodine value ca. 135) with a mixture of sodium and barium hydroxides, a 35% fraction could be separated with an iodine value of 165; and that by similarly treating fish oil fatty acids having an iodine value of 202, a 50% fraction could be separated with an iodine value of 283.

[57] S. H. Bertram, Z. deut. Öl- u. Fett-Ind., 45, 733–736 (1925); Chem. Weekblad, 24 226–229 (1927).
[58] T. P. Hilditch and C. H. Lea, J. Chem. Soc., 1927, 3106–3117.
[59] J. D. Fitzpatrick and L. D. Myers (to Emery Industries), U. S. Pat. 2,369,036 (1945).
[59a] L. H. Dunlap, L. V. Hassel, and J. L. Maxwell, J. Am. Oil Chem. Soc., 27, 361–366 (1950).
[60] E. Schlenker, U. S. Pats. 1,862,037 (1932) and 1,948,683 (1934).
[60a] J. H. Sanders (to Procter & Gamble Co.), U. S. Pat. 2,485,779 (1949).
[61] R. Nicholsen and M. W. Formo, J. Am. Oil Chem. Soc., 26, 329–331 (1949).

The conversion of mixed fatty acids to lead soaps or other metal soaps prior to fractional crystallization is a common laboratory practice which, however, merely enables the separation to be carried out at a higher temperature than if the acids were crystallized, and does not improve the efficiency of the separation.

The treatment of oils with liquid sulfur dioxide, to convert monoethenoid acids to high-melting *trans*-isomers, followed by fractional crystallization to remove high-melting glycerides, has been suggested as a means of producing an oil fraction of improved drying properties.[61a]

A highly interesting new technique for the fractionation of fatty acids[61b] involves treatment of the acids in solution with urea, which will form crystalline addition compounds with the more saturated members. After separation by filtration, the addition compounds are broken down to yield free acids and urea solution suitable for re-use, by treatment with water. This method is said to be particularly suitable for the elimination of polyethenoid acids from mixtures with oleic acid and saturated acids. It appears to depend upon the ability of straight chains to penetrate the urea lattice, where they are held by quasi-adsorptive forces. Branched chains and chains in which much irregularity is introduced by the presence of *cis*-double bonds are unable to so penetrate and do not form addition compounds.

2. CHROMATOGRAPHY

Chromatographic separation (selective adsorption from solution in a column packed with solid adsorbent), which has found a limited commercial use on certain other materials,[62] has apparently not been applied to fats and oils. However, the method is a common laboratory tool, and is of some interest because of its remarkable effectiveness in isolating fat components which are difficult or impossible to separate cleanly by other means.

Fatty acids or glycerides or other fatty acid esters may be separated chromatographically either on the basis of the degree of unsaturation or chain length.[63,64] Among the more recent and more effective uses of the technique, there may be mentioned the separation of linseed oil into glyceride fractions containing 4, 5, 6, 7, 8, and 9 double bonds, by

[61a] H. I. Waterman, C. van Vlodrop, and J. Hannewyk, *Research*, 1, 183–185 (1948).
[61b] F. Bengen, German Pat. application O. Z. 12.438 (1940). See also H. Schlenk and R. T. Holman, *Science*, 112. 19–20 (1950); W. J. Zimmerschied, R. A. Dinerstein, A. W. Weitkamp, and R. F. Marschner, *Ind. Eng. Chem.*, 42, 1300–1306 (1950); H. A. Newey, E. C. Shokal, A. C. Mueller, and T. F. Bradley, *ibid.*, 42, 2538–2541 (1950).
[62] R. Williams, Jr., and J. V. Hightower. *Chem. Eng.*, 55. No. 11, 133–138 (1948).
[63] H. P. Kaufmann, *Fette u. Seifen*, 46, 268 (1939); Z. *angew. Chem.*, 53. 98 (1940).
[64] H. G. Cassidy, *J. Am. Chem. Soc.*, 62, 3073 (1940); 63, 2735 (1941). H. G. Cassidy and S. E. Wood. *ibid.*, 63, 2628 (1941).

Walker,[65] the fractionation of mixtures of ethyl stearate, oleate, linoleate, and linolenate, by Dutton and Reinbold,[66] and the preparation of highly pure methyl linoleate by Swift *et al.*,[67] methyl linoleate and linolenate by Riemenschneider *et al.*,[68] and methyl isolinoleate by Lemon.[69] However, the greatest usefulness of chromatography in dealing with fats has been in the separation of nonfatty constituents which can scarcely be isolated in a highly pure form by any other method. It is effective in dealing with sterols (including vitamin D),[70] tocopherols,[71] vitamin A,[72] and carotenoid and other pigments.[73] Phosphatides can also be separated,[74] as well as mixtures of mono-, di-, and triglycerides,[75] and *cis*- and *trans*-isomers of fatty acids.[75]

F. Recovery of Minor Constituents

The separation from crude vegetable oils of phosphatides, to be marketed as commercial lecithin, has been dealt with in Chapters XV and XVI. In addition, there is a large commercial production of vitamin A concentrates from fish liver oils, for the fortification of margarine and for pharmaceutical use, and a smaller but significant production of purified cholesterol from animal fats, of purified vegetable sterols, from soybean and other vegetable oils, of tocopherol concentrates from vegetable oils (all used in pharmaceuticals), and of beta-carotene, from palm oil, for addition to margarine or use in vitamin preparations.

Older methods for producing concentrates of vitamin A or other nonfatty and unsaponifiable constituents follow the common laboratory procedure of saponifying the oil and washing out the soaps from a solution of the residual material with water. In recent years saponification methods have been supplanted to a considerable extent by methods which effect a recovery of desired minor constituents from the untreated oil. Of these, molecular distillation was the first used and is still much the most important. However, effective techniques are now available based on liquid-liquid extraction and fractional crystallization. In the case of

[65] F. T. Walker, *J. Oil Colour Chem. Assoc.*, *28*, 119–134 (1945).
[66] H. J. Dutton and C. L. Reinbold, *J. Am. Oil Chem. Soc.*, *25*, 120–124 (1948).
[67] C. E. Swift, W. G. Rose, and G. S. Jamieson, *Oil & Soap*, *20*, 249–250 (1943).
[68] R. W. Riemenschneider, S. F. Herb, and P. L. Nichols, Jr., *J. Am. Oil Chem. Soc.*, *26*, 371–374 (1949).
[69] H. W. Lemon, *Can. J. Research*, B*27*, 605–609 (1949).
[70] See, for example, K. Ladenburg, E. Fernholz, and E. S. Wallis, *J. Org. Chem.*, *3*, 294 (1938).
[71] See, for example, J. G. Baxter and C. D. Robeson (to Distillation Products, Inc.), U. S. Pat. 2,379,420 (1945).
[72] See, for example, P. Karrer, R. Morf, and K. Schöpp, *Helv. Chim. Acta*, *14*, 1036, 1431 (1931).
[73] See, for example, L. Zechmeister in H. Schönfeld, ed., *Chemie u. Technologie der Fette u. Fettprodukte*. Vol. I, Springer, Vienna, 1936, pp. 162–163.
[74] H. R. Kraybill, P. H. Brewer, and M. H. Thornton (to Purdue Research Foundation), U. S. Pat. 2,353,571 (1944).
[75] H. P. Kaufmann and W. Wolf, *Fette u. Seifen*, *50*, 519–521 (1943).

vitamin A recovery, the newer methods have the advantage of producing the vitamin largely in the natural ester form, rather than in the form of the free alcohol, which is said[76] to be less stable. A recent process of considerable interest substitutes interesterification of the fat with methyl or ethyl alcohol for the conventional saponification procedure. After the glycerides are converted to monoesters, they may be readily distilled from the unesterified residue by ordinary distillation methods. Very recently, methods have been developed for the commercial manufacture of relatively cheap synthetic vitamin A, and it appears probable that these will eventually render some, if not all, of the natural vitamin A recovery processes obsolete.

Molecular distillation is carried out by passing oil through the still at such a temperature that the component to be recovered will distill more rapidly than other less volatile components or than the triglycerides making up the bulk of the oil. Where more than one component is to be recovered, this involves successive passages of oil through the still at a series of ascending temperatures. With respect to volatility, certain common constituents stand in the following ascending order:[77]

1. Free fatty acids
2. Vitamin A (in the form of the free alcohol)
3. Sterols, including vitamin D (in the free form)
4. Tocopherols
5. Vitamin A in esterified form
6. Triglycerides

Pigments of the oil are divided between those that distill less readily than most of the above components, but more readily than triglycerides (including carotenoid pigments), and others that are so lacking in volatility that the glycerides may be distilled, leaving the pigments in a small residue. Many of the latter are probably decomposition and polymerization products that do not originally exist as such in the oil, but are formed when the oil is heated. Phosphatides also tend to remain largely in the residue. In practice, tocopherols are taken off at about 160–190°C. (320–374°F.), and vitamin A esters at about 200–250°C. (392–482°F.). Triglycerides containing C_{16} and C_{18} fatty acids do not distill very rapidly below a temperature of about 200°C.

As noted above, molecular distillation is used on a large scale for the separation of vitamin A concentrates from fish liver oils and tocopherol concentrates from soybean, wheat germ, and other vegetable oils, and for the distillation of monoglycerides. For the production of tocopherol concentrates, the preferred raw material is the fatty distillate or scum resulting from the steam deodorization of vegetable oils, which may

[76] K. C. D. Hickman and A. O. Tischer, U. S. Pat. 2,169,195 (1939).
[77] K. C. D. Hickman, Chem. Revs., 34, 51–106 (1944).

contain several per cent of tocopherols. Methods for the pretreatment of deodorizer scums to reduce tocopherol oxidation products, etc., are covered in a series of patents issued to Hickman and associates.[78] Tocopherol concentrates may also be produced by fractionally crystallizing out glycerides and sterols in a suitable solvent,[79-81] and liquid-liquid extraction[79,82] and alcoholization-distillation[83] processes have been claimed for tocopherol recovery. In dealing with certain materials, saponification may be a useful auxiliary to molecular distillation, liquid-liquid extraction, or fractional crystallization.[84]

Liquid-liquid extraction with propane[85] is also used commercially for the preparation of vitamin A concentrates, although much of the product on the market is still made by the technique of saponification followed by small-scale liquid-liquid extraction. Liquid propane extraction has been patented for the manufacture of beta-carotene concentrates from palm oil.[86]

Details of the methods used commercially for the separation of sterols are not generally a matter of public record, although from the patent literature[87] it may be presumed that the usual method involves saponification and extraction of the sterols from a mixture of soap and inert porous material with acetone. Soapstock from the alkali refining of edible soybean oil is used as a raw material for vegetable sterol manufacture.

Methods have been patented for recovering vitamin A and sterols,[83] and carotene[88] by alcoholization followed by distillation.

By repeatedly distilling vegetable oils and taking out an intermediate cut at about 240°C. (464°F.), glycerides may be obtained which are almost free of nonglyceride impurities.[89] Only limited fractionation of the glycerides may be achieved by molecular distillation.[89]

[78] K. C. D. Hickman et al. (to Distillation Products, Inc.), U. S. Pats. 2,349,269-78 (1944).
[79] K. C. D. Hickman (to Distillation Products, Inc.), U. S. Pat. 2,349,275 (1944).
[80] J. D. Cawley (to Distillation Products, Inc.), U. S. Pat. 2,375,078 (1945).
[81] W. S. Singleton and A. E. Bailey, Oil & Soap, 21, 224-226 (1944).
[82] L. O. Buxton (to National Oil Products Co.), U. S. Pats. 2,396,680-1 (1946).
[83] W. R. Trent (to Colgate-Palmolive-Peet Co.), U. S. Pat. 2,432,181 (1947).
[84] K. C. D. Hickman (to Distillation Products, Inc.), U. S. Pat. 2,349,270 (1944).
[85] L. J. Van Orden (to M. W. Kellogg Co.), U. S. Pat. 2,394,968 (1946).
[86] H. B. Larner (to M. W. Kellogg Co.), U. S. Pat. 2,432,021 (1947).
[87] See P. L. Julian, E. W. Meyer, and N. F. Kruse (to Glidden Co.), U. S. Pat. 2,218,971 (1940); N. F. Kruse, E. B. Oberg, W. E. Mann, H. R. Kraybill, and K. E. Eldridge (to Central Soya Co. and Purdue Research Foundation), U. S. Pat. 2,296,794 (1942); E. B. Oberg and A. W. Kleinsmith (to Central Soya Co.), U. S. Pat. 2,330,140 (1943).
[88] E. W. Eckey (to Procter & Gamble Co.), U. S. Pat. 2,460,796 (1949).
[89] H. W. Rawlings, Oil & Soap, 16, 231-232 (1939). R. W. Riemenschneider, C. E. Swift, and C. E. Sando, ibid., 17, 145-148 (1940). S. B. Detwiler, W. C. Bull, and D. H. Wheeler, ibid., 20, 108-122 (1943). A. E. Bailey, G. D. Oliver, W. S. Singleton, and G. S. Fisher, ibid., 20, 251-255 (1943). W. S. Singleton and A. E. Bailey, ibid., 21, 157-159 (1944).

POLYMERIZATION, ISOMERIZATION, AND RELATED PROCESSES

A. Polymerization

1. POLYMERIZATION OF DRYING OILS

Both the theory and practice of the polymerization of drying oils have been treated at some length in Chapter XII. Only the mechanics of the process remain to be considered here.

A somewhat sharp distinction may be made between polymerization effected largely through the agency of heat, and polymerization in which oxidation plays a prominent role. Heat polymerization is considered to produce direct carbon-to-carbon linkages between the unsaturated acid chains, whereas polymerization accompanied by oxidation presumably occurs to a considerable extent through the establishment of carbon-oxygen-carbon linkages.

Most of the polymerized oil produced at present is utilized in protective coatings. For the manufacture of this class of products heat-polymerized oils are generally, although by no means always, preferred. On the other hand, the linoleum industry, which is the second largest user of polymerized oils, requires a highly oxidized polymer.

(a) Practice in Heat Polymerization or Oil Bodying

Formerly, purely heat-polymerized oils were not generally available. The common practice was to polymerize the oil by heating in an open kettle, with free access to the air; hence in the operation the oil invariably underwent considerable oxidation. Oils are now often heat-treated in a closed vessel under a vacuum or an atmosphere of carbon dioxide, with very little oxidation taking place.

The kettles used for heat bodying or polymerizing drying oils vary extremely in capacity, design, and method of operation. The cruder installations consist simply of open cylindrical kettles, unstirred, or stirred by hand, and heated by a direct fire. The most modern kettles are closed, provided with agitators, and heated by electric resistance heaters, circulated hot mineral oil, or, more commonly, the condensation of Dowtherm vapors.

To avoid oxidation during the course of polymerization, where this is desired, connections are provided for blanketing the oil with carbon dioxide or flue gas, or the batch may be kept under a vacuum of about 20–30 mm. In the event that an inert gas is used, it may be continuously bubbled through the oil mass, or merely flooded over the surface of the batch. In some cases where an inert gas is used, a partial vacuum is also maintained on the kettle. As compared with other processing vessels used in the oil and fat industry, the kettles are usually small. Their size is limited by difficulties in providing sufficient heat-transfer surface for reasonably rapid heating. In order to provide free circulation of the relatively viscous oil in the kettle, heating coils are avoided; hence the heat must be transferred entirely through the kettle walls. The largest kettles have a capacity of 500 to 1000 gallons, although kettles of 100 to 250 gallons capacity are more common. They are preferably constructed of metals such as stainless steel, or nickel-clad steel, to avoid contaminating and darkening the oil with iron soaps.

For the best control of the bodying operation it is desirable to have some means of quickly reducing the temperature of the batch, and thus arresting the reaction, when the desired degree of polymerization is attained. If the kettle is heated by Dowtherm vapors, the batch may be cooled by the circulation of cold Dowtherm liquid through the heating jacket. The polymerization reaction evolves considerable heat, particularly during the earlier stages, which is commonly utilized in bringing the batch up to the top temperature that is desired. However, cooling to remove heat of reaction may be necessary. Electrically heated kettles are often provided with an auxiliary cooling tank, into which the hot batch may be dropped. Tung and oiticica oils polymerize very rapidly in the latter stages of bodying; hence there is much danger of gel formation in the production of heavily bodied products from these oils, unless the heating is very accurately controlled. In the polymerization of such oils it may be necessary to check the reaction by adding a portion of cold oil. Small batches of oil can of course be cooled more quickly than large batches.

The degree to which an oil is polymerized is measured in terms of its viscosity, and the reaction may, therefore, be followed by periodically withdrawing samples and checking the viscosity. As polymerization proceeds, the change of viscosity in unit time becomes progressively greater, a plot of bodying time against kinematic viscosity yielding a curve of an approximately exponential form. If the temperature of the batch is maintained constant during the period of observation, and the time is plotted against the logarithm of the viscosity, there will usually be obtained either a substantially straight line, or a series of two or three straight lines.

Viscosity–time curves for a number of drying oils bodied at different temperatures are recorded in Figures 159 and 160.[1-8] The rate of bodying increases quite rapidly with the temperature, doubling for each increment of about 25°F. Von Mikusch[5] calculated the doubling interval to
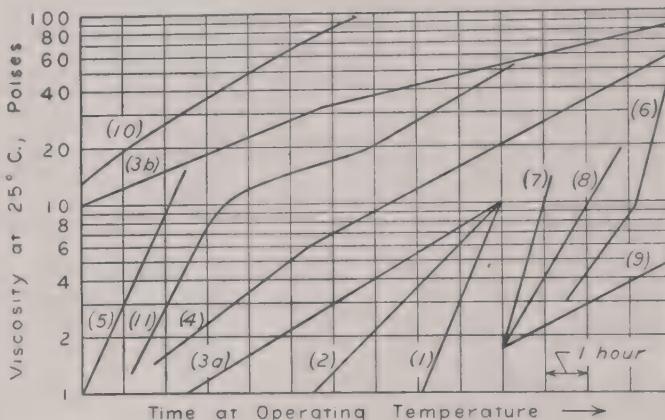
Fig. 159. Viscosity *vs.* bodying time in the heat bodying of various drying oils:

(*1*) Linseed oil, commercial, 625°F.[1]
(*2*) Linseed oil, commercial, 575°F.[1]
(*3*) Linseed oil, commercial, 550°F.[1]
(*4*) Linseed oil, commercial, 565°F.[2]
(*5*) Soybean oil, laboratory, 600°F.[3]
(*6*) Dehydrated castor oil, commercial, 550°F.[4]
(*7*) Dehydrated castor oil, laboratory, 590°F.[5]
(*8*) Dehydrated castor oil, laboratory, 560°F.[5]
(*9*) Dehydrated castor oil, laboratory, 500°F.[5]
(*10*) Sardine oil, I.V. 201, clear 8 hours at 32°F., commercial, 555°F.[6]
(*11*) Menhaden oil, I.V. 179, commercial, 565°F.[7]

be about 24°F. for linseed oil in the range of 550–625°F., and about 27°F. for dehydrated castor oil in the range 500–590°F. According to Cannegieter,[8a] the effect of temperature on the bodying rate, and the heat of polymerization are interrelated.

[1] B. P. Caldwell and J. Mattiello, *Ind. Eng. Chem., 24,* 158–162 (1932).
[2] J. Mattiello and L. T. Work, *Natl. Paint, Varnish Lacquer Assoc. Circ. No. 502* (1936).
[3] A. J. Lewis, *private communication,* 1944.
[4] J. F. Gerkens and V. A. Kildare in *Protective and Decorative Coatings.* Edited by J. J. Mattiello, Vol. III, Wiley, New York, 1943, pp. 82–85.
[5] J. D. Von Mikusch, *Ind. Eng. Chem., 32,* 1061–1069 (1940).
[6] Los Angeles Production Club, *Natl. Paint, Varnish Lacquer Assoc. Circ. No. 548,* 263–271 (1937).
[7] L. T. Work, C. Swan, A. Wasmuth, and J. Mattiello, *Ind. Eng. Chem., 28,* 1022–1024 (1936).
[8] S. O. Sorensen, C. J. Schumann, J. H. Schumann, and J. Mattiello, *Ind. Eng. Chem., 30,* 211–215 (1938).
[8a] D. Cannegieter, *Centraal Inst. Material Onderzoek Afdel. Verf. Circ.,* No. 51, 1946; *Paint Oil Chem. Rev., 110,* No. 4, 17–18, 38, 40–41 (1947).

The curves of Figures 159 and 160 give an indication of the actual times required to heat-body different oils at different temperatures. In general, the atmosphere in which the operation is carried out does not appear to have any large effect upon the bodying rate, nearly equivalent times being required for bodying in air, under carbon dioxide, and under a vacuum. In practice, a considerable time will of course be required to bring the batch to operating temperature. Some degree of bodying will occur during the heating period, and allowance must be made for this in estimating the total time for the operation. Methods for calculating the heating equivalent of the warm-up period, in terms of time at the top
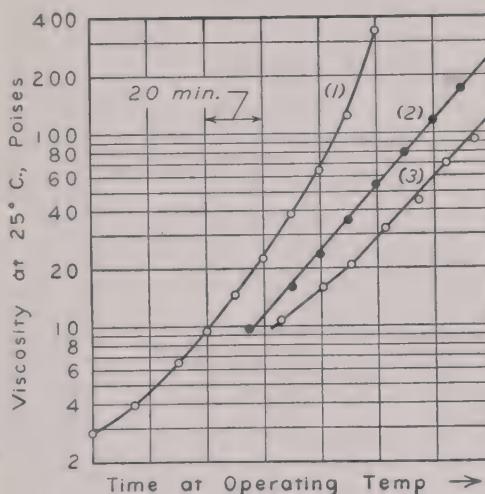
Fig. 160. Viscosity *vs.* bodying time in the heat bodying of conjugated acid oils:[8]   (*1*) Tung oil, in air, 450°F. (*2*) Oiticica oil, in air, 450°F. (*3*) Oiticica oil, in carbon dioxide, 450°F.

temperature, have been given by Turkington, Shuey, and Schechter,[9] and Von Mikusch.[5]   The Von Mikusch formula is particularly useful:

$$H = 1.44 \; D/c$$

where H = heating equivalent in minutes; D = doubling interval (see above); and c = heating rate in degrees F. per minute. This formula assumes a constant heating rate, and a constant doubling interval for the oil. It is applicable to cooling, as well as heating, that is:

$$C = 1.44 \; D/c'$$

where C = cooling equivalent and c' = cooling rate.

⁹ V. H. Turkington, R. C. Shuey, and L. Schechter, *Ind. Eng. Chem.*, *30*, 984–990 (1938).

Following the convention adopted by Cannegieter,[8a] the bodying rate for a given oil at a specified temperature may be stated in terms of change in log viscosity with change in time according to the following formula:

$$K = (\log v_2 - \log v_1)/(t_2 - t_1)$$

where K is a bodying rate constant, and v_1 and v_2 are viscosities in poises at times t_1 and t_2 (in minutes), respectively. Values of K at 300°C. are 0.0032 to 0.0057 for linseed oil, and 0.0088 for dehydrated castor oil; values at 250°C. are 0.0007 (average) for linseed oil, and 0.054–0.055 for tung oil.

Attempts have been made to develop a formula for calculating K in terms of fatty acid composition for linseed oil, soybean oil, or other oils whose unsaturated fatty acids consist of linolenic, linoleic, and oleic. In working with a number of oils, fractionated oils, and oil blends at 585°F., Anderson and Porter[9a] obtained fairly smooth (but not linear) curves relating K to fatty acid composition in the range 0.5–100 poises when the contents of linolenic, linoleic, and oleic acids were given the relative weights of 2.0, 1.6, and 0.6, respectively. The calculated values for K were average values which in most cases applied to three distinct sections of the bodying curve, each of which had a slightly different slope. Actually, linoleic acid was observed to polymerize more rapidly, relative to linolenic acid, over the second section of the curve than over the first, whereas the effect of oleic acid was greatest in the last stage of bodying preceding gelation. As a result, with oils relatively high in linolenic acid, e.g., linseed oil, the first linear section of the bodying curve had a greater slope than the second, whereas with oils relatively high in linoleic acid and low in linolenic acid, e.g., corn oil, the relative slopes of the two sections were reversed. In all cases the bodying rate appeared to depend purely upon the fatty acid composition of the oil, and to be independent of its glyceride composition.

Taking into account the bimolecular character of the reaction, Powers[9b] has proposed the following relationship, which also gives a good correlation at 585°F.:

$$K = (4.5 \text{ linolenic acid content} - 2 \text{ linoleic acid content})^2/1000$$

In commercial practice, linseed oil is usually bodied at some temperature between about 560° and 625°F. Soybean oil bodies more slowly than linseed oil, and hence requires a high temperature, e.g., 600° to 625°F. Dehydrated castor oil is bodied at lower average temperatures than linseed oil, e.g., at about 550°F. Fish oils are also bodied at about this temperature. Polymerization is so rapid in tung and oiticica oils that these are not generally bodied at temperatures above about 450°F.

[9a] L. V. Anderson and J. V. Porter, *Ind. Eng. Chem.*, *41*, 741–749 (1949).
[9b] P. O. Powers, *J. Am. Oil Chem. Soc.*, *27*, 468–472 (1950).

In selecting the temperature at which polymerization is to be conducted, a balance must be struck between the desirability of operating at a high temperature, to decrease heating costs and increase the daily capacity of the kettles, and the desirability of operating at a low temperature, to avoid excessive losses through volatilization and to obtain a better oil. Oils bodied at a relatively low temperature are lighter in color and lower in acidity than oils bodied at a high temperature, and are generally considered to yield more durable paints and varnishes. They also are less inclined to form products which liver in the package.[2]

When bodied in contact with the air, linseed oil darkens considerably and also increases progressively in free fatty acid content, as bodying is continued. In large-scale tests in which linseed oil was bodied in air at 535°, 575°, and 600°F., Mattiello and Work[2] found that the acid numbers of the oils at a viscosity of 60 poises were, respectively, about 6, 10, and 14. In corresponding tests conducted under vacuum the acid number did not increase progressively, and was in no case greater than about 2 in the finished product. The oil also darkened less under vacuum than in the air. However, linseed oil developed a higher acidity when bodied under carbon dioxide than when bodied in air. Vacuum-bodied oils are said to have practically no tendency to liver.[2]

Tung oil becomes lighter during polymerization and does not increase in acidity even when exposed to the air during the operation. The tendency of oiticica oil to increase in acidity during bodying is but slight. Sardine oil or other fish oils exhibit a somewhat peculiar behavior in heat bodying. If sardine oil, whether winterized or unwinterized, is bodied to a viscosity greater than about 10 poises, it is inclined to form a so-called polymer cloud, and precipitate solid gel particles.[6] This characteristic of the oil may be presumed to be due to the peculiar glyceride composition of marine oils, or in other words, to the fact that these oils contain very highly unsaturated and reactive glycerides mixed with a large proportion of other glycerides which are relatively unreactive. Polymerization of such a mixture would naturally be expected to proceed unevenly.[10] For the production from fish oils of heavy-bodied oils not subject to clouding, it is recommended[6] that the oil be first heat-bodied to a viscosity of about 9 poises, and then further increased in viscosity by air blowing. A temperature of 535°F. was suggested as optimum for bodying fish oils. At this temperature the oil was observed to increase in molecular weight more rapidly than at 555°F., and to develop but little acidity.

[10] In this connection, see also H. N. Brocklesby, *The Chemistry and Technology of Marine Animal Oils*, Fisheries Research Board of Canada, Ottawa, 1941, pp. 127–128. Brocklesby considers that the "polymer cloud" is composed at least in part of precipitated glycerides of a low degree of unsaturation, which become insoluble in the polymerized oil. He points out that there may well be rearrangement of the glycerides in the oil during bodying, to produce fully saturated glycerides.

A considerable loss of oil is invariably incurred during heat bodying, through decomposition and volatilization of the decomposition products. The actual loss in any case will depend upon the temperature of operation, the nature of the oil, the degree to which it is bodied, and whether the volatile products are continuously removed or partially condensed and returned to the kettle. Losses as high as 10% or higher are often recorded in the manufacture of heavy-bodied products from oils which polymerize with relative slowness.

A number of special methods have been patented for the rapid and continuous polymerization of drying oils.

(b) Catalysts for Heat Polymerization

There are a number of substances which promote polymerization when added to unsaturated oils. Some of these are effective in small amounts, and appear to act catalytically. Others very definitely enter into permanent chemical combination with the oil, and may be incorporated into the oil in considerable quantity.

The leading example of a polymerizing agent which reacts chemically with the oil, to establish cross linkages between unsaturated fatty acid chains, is furnished by sulfur and certain of its compounds The use of these in the manufacture of factice has been outlined in Chapter XIII. Sulfur compounds have also been patented as catalytic polymerization agents. However, sulfur inhibits the drying of oils, and may be used to prevent gelation in the heat bodying of tung oil. Gardner[11] employs sulfur or sulfur-containing compounds in the bodying of tung oil, to prevent gelation, and removes the sulfur at the conclusion of the operation by reaction with copper. Harper[12] uses selenium for the same purpose. Parkin[13] has patented the use of diaryl and dialkyl disulfides.

Hydrogen chloride is mentioned by a number of writers as a catalytic agent for the heat bodying of oils. Long and Ball[14] have patented a class of resinous drying oil products in which chlorine is combined. Various metallic chlorides are used by Stoddard, Geiger, and Burgess[15] for polymerizing drying oils. Boron fluoride has received particular attention as an assistant for the polymerization of fatty oils to be used with petroleum products in compounding lubricants.[16] Rheineck and Crecelius[17] claim silicotungstic acid and other tungstic acids as catalytic agents for oil bodying.

[11] H. A. Gardner, U. S. Pat. 1,986,571 (1935).
[12] W. J. Harper, U. S. Pat. 2,152,642 (1939).
[13] F. P. Parkin (to Minnesota Linseed Oil Paint Co.), U. S. Pat. 2,263,887 (1941).
[14] J. S. Long and G. L. Ball, U. S. Pat. 2,044,007 (1936).
[15] W. B. Stoddard, T. H. Geiger, and L. M. Burgess, U. S. Pat. 1,924,524 (1933).
[16] E. Eichwald, U. S. Pat. 2,160,572 (1939); J. M. Whitely and L. B. Turner (to Standard Oil Development Co.), U. S. Pat. 2,260,417 (1941).
[17] A. E. Rheineck and S. B. Crecelius (to Devoe & Reynolds Co.), U. S. Pat. 2,345,358 (1944).

A number of metallic catalysts for polymerization have been patented, in addition to the metallic dryers commonly used in boiled oils. A novel method of incorporating metallic dryers such as nickel, cobalt, iron, etc., in the form of carbonyls, is revealed by Ambros et al.[18]

From a practical standpoint, however, much the most important polymerization catalysts are of the type patented by Sorensen and Konen,[19] which consist of organic compounds containing at least three aromatic rings, including anthroquinone, phenanthrene, anthracene, and their derivatives. A common catalyst of this type is beta-methyl anthroquinone. There is good evidence[20] that these are actually isomerization catalysts, which assist in moving adjacent double bonds to conjugated positions, to permit linkage of fatty acid chains by a Diels-Alder reaction (see page 414). Schwarcman claims the use of phenanthrenelike compounds, including chrysene, retene, and picene, which have been oxidized sufficiently to contain ketone and hydroxyl groups,[21] and also polycyclic aromatic compounds containing one carboxyl group and at least two hydroxyl groups, for example, diphenolcarboxyl anthracene.[22]

Waterman and co-workers[23] have shown that sulfur dioxide is a powerful polymerization catalyst. In this case, the action of the catalyst is definitely to promote isomerization, as extensive "activation" or conjugation of the oil can be demonstrated prior to polymerization.[24]

For the polymerization of unsaturated fatty acids at very high temperatures (330–360°C. or 626–680°F.), Goebel[24a] found catalysts to have relatively little effect on the reaction rate. Of a number of catalysts tested, mercuric acetate and Raney nickel were both more effective than anthroquinone.

2. Oxidation Polymerization of Oils

Relatively simple equipment is required for the manufacture of blown oils, which are generally processed at a temperature under about 250°F. The operation consists simply of blowing a vigorous current of air through the heated oil until the desired viscosity is attained. If the operation is prolonged, the reaction may become sufficiently exothermic to require the

[18] O. Ambros, H. Reindel, J. Eisele, and J. Stoehrel, U. S. Pat. 1,891,203 (1932).
[19] S. O. Sorensen and J. C. Konen (to Archer-Daniels-Midland Co.), U. S. Pat. 2,213,935 (1940).
[20] See E. C. Terrill, Oil & Soap, 23, 339–344 (1946); L. B. Falkenburg, W. De Jong, D. P. Handke, and S. B. Radlove, J. Am. Oil Chem. Soc., 25, 237–243 (1948).
[21] A. Schwarcman (to Spencer Kellogg & Sons), U. S. Pat. 2,207,686 (1940).
[22] A. Schwarcman (to Spencer Kellogg & Sons), U. S. Pat. 2,230,470 (1941).
[23] H. I. Waterman and C. van Vlodrop (to Imperial Chemical Industries Ltd.), Brit. Pat. 480,677 (1938), U. S. Pat. 2,188,273 (1940); H. I. Waterman, D. P. A. Hak, and B. Pennekamp, J. Am. Oil Chem. Soc., 26, 393–394 (1949).
[24] H. I. Waterman, C. van Vlodrop, and M. J. Pfauth, Research, 1, 186–192 (1948). J. H. de Boer, J. P. H. Houtman, and H. I. Waterman, Koninkl. Nederland. Akad. Wetenschap. Proc., 50, 1181–1188 (1947).
[24a] C. G. Goebel, J. Am. Oil Chem. Soc., 24, 65–68 (1947).

batch to be cooled, in order to maintain the proper temperature. Oils are blown to various degrees of polymerization, according to their particular uses. In some cases, particularly where it is desired to reduce the time required for heat bodying, or where a surface-active oil is desired, drying oils are first slightly polymerized by blowing, and then heat-polymerized. For some purposes, a certain degree of oxidation is desired during heat bodying. The practice of "top-firing," or heating in an open kettle while burning off the volatile products of reaction is still followed in polymerizing oils for certain varieties of printing inks.

It is to be emphasized that the physical characteristics and chemical behavior of blown oils are markedly dependent upon the temperature at which blowing is conducted. According to Hess and O'Hare,[24b] there are for linseed oil three critical temperature regions, which are respectively above 130°C., between 130° and 84°C., and below 84°C. For oils that are to be subsequently heat bodied, relatively high blowing temperatures may be used, but low temperatures are required to produce the oils of high oxygen content that are required for certain special products. In general, as the oxygen content of the oil increases it becomes decreasingly compatible with hydrocarbons and with other oils, and increasingly compatible with polar solvents. Oils blown to a viscosity of 2.5–5.0 poises at low temperature (50–70°C.) are soluble in natural and synthetic resins, and linseed oil similarly blown until it forms a gel on cooling is compatible with nitrocellulose and nitrocellulose solvents.[25]

The solid "linoxyn" used in the manufacture of linoleum must be almost entirely oxygen polymerized, at a temperature not in excess of about 120°F. The special methods used for making this product are described in Chapter XIII.

Caldwell and Price[25a] have reported in detail the effect of air blowing on a 4500-gallon batch of rapeseed oil over a period of 32 hours. Blowing was started at 115°C. (239°F.) and heat of reaction was allowed to carry the temperature to 150°C. (302°F.), after which the batch was maintained at a constant temperature by the circulation of water through a cooling jacket. Within 26–32 hours the Saybolt viscosity at 40°C. increased from 3.9 to 345 seconds, the iodine value decreased from 95.3 to 64, the saponification value increased from 173 to 199, the refractive index at 20°C. increased from 1.4730 to 1.4806, the specific gravity at 40°C. increased from 0.900 to 0.957, the acid value increased from 2.17 to 8.30, and the heat of combustion decreased from 9568 to 8946 cal. per gram. Rapid change in these various characteristics of the oil began at the end of 10–12 hours, which time also coincided with the appearance

[24b] P. S. Hess and G. A. O'Hare, *Ind. Eng. Chem.*, *42*, 1424–1431 (1950).
[25] W. L. Taylor, *J. Am. Oil Chem. Soc.*, *27*, 472–476 (1950).
[25a] B. P. Caldwell and R. B. Price, *Ind. Eng. Chem.*, *23*, 1463–1466 (1931).

of an appreciable heat of reaction. The oil formed a sticky gel when cooled.

In an article dealing with the commercial blowing of drying oils, Taylor[25] has given complete operating and analytical data on the treatment of raw linseed oil at relatively high temperatures (up to 138°C.) to produce a light blown product, the treatment of raw linseed oil at lower temperatures (71–82°C. after the end of the induction period) to produce a heavy bodied product, and the treatment of degummed soybean oil at similar temperatures to produce a heavy bodied oil. The light bodied linseed oil was finished in 200 minutes with a specific gravity of 0.9502 (0.9334 originally), a refractive index at 25°C., of 1.4815 (1.4793 originally), and a viscosity of about 1 poise. The acid number increased from 2.2 to 3.3 and the Gardner color decreased from 12 to 9. Blowing of the heavy bodied linseed oil product required 45 hours, during which time the refractive index at 25°C. increased from 1.4787 to 1.4869, acid number increased from 2.1 to 5.5, the Gardner color decreased from 12 to 8, and the viscosity increased from 0.5 to 30.6 poises. A blowing time of 166 hours was required to raise the viscosity of the soybean oil from 0.5 to 29.4 poises and the refractive index at 25°C. from 1.4713 to 1.4791. The acid number increased from 0.9 to 8.5, the peroxide number increased from 3.6 to 290.8, and the hydroxyl number increased from zero to 61.1.

According to Taylor,[25] heavy bodied blown linseed oils are frequently finished at a viscosity of Z-1 to Z-2, inasmuch as after-polymerization in the package will commonly increase the viscosity to Z-2 to Z-3. On the other hand, fish oils and semi-drying vegetable oils are more frequently blown to viscosities of Z-4 to Z-6, or even higher.

In laboratory experiments in the blowing of rapeseed oil, Caldwell and Dye[25b] found that the humidity of the blowing air had no effect on the rate of viscosity increase, although at blowing rates of 6, 12, and 18 volumes of air per hour per unit volume of oil there was a progressive increase in the bodying rate with increase in the air flow at temperatures in the range 154–186°C. (310–367°F.). The reaction was mildly catalyzed by the addition of 1–2% unsaturated free fatty acids or previously blown oil, or by the presence of 0.1% aluminum, lead, or magnesium in the form of metal soaps. The most effective catalyst, aluminum oleate, reduced the time to attain a Saybolt viscosity of 335–350 from 10 to 7 hours. Without a catalyst, peroxides were found to be at a maximum in the oil at the point when the viscosity, iodine value, etc., were changing most rapidly; when catalysts were present, no peroxides could be detected. In all cases the oil was virtually peroxide-free during the latter stages of polymerization.

In an experiment in which linseed oil was blown with air at 110°C.

[25b] B. P. Caldwell and G. H. Dye, *Ind. Eng. Chem.*, **25**, 338–342 (1933).

(230°F.) O'Hare et al.[26] found that after an induction period of about two hours the logarithm of the viscosity increased linearly with the reaction time, as in the thermal polymerization of drying oils (Fig. 162). In a similar experiment in which sardine oil was blown at 220°F. (104°C.), O'Hare and Withrow[27] found a linear relationship between log viscosity and time (in successive stages), but no induction period. A difference in the behavior of the two oils is to be anticipated, in view of the presence of natural antioxidants in the vegetable oil.

In the practical blowing of vegetable oils, the time required is more dependent upon the length of the induction period which precedes rapid oxidation than upon the rate of reaction thereafter.[24b] Often, to shorten the processing time, the temperature is raised during the induction period, and lowered afterwards.

Blowing is often conducted in the presence of dryers, but the presence of these, even at low temperatures, is inclined to give the oil the characteristics of a high temperature blown product.[25]

In the preparation of oxidation-polymerized or blown oils, the viscosity of the oil is scarcely an adequate characteristic for control of the reaction, inasmuch as concurrent thermal polymerization may increase the viscosity without producing a satisfactorily oxygenated material. Inasmuch as the dielectric constant of a blown oil such as linseed oil increases regularly with the oxygen content, from 3.20–3.25 originally, to about 5.00 at an oxygen content of 17.5–18.5%, whereas thermal polymerization is without effect on the dielectric constant, determinations of this characteristic have been recommended as a control measure.[26-28]

3. RELATIONSHIP OF VISCOSITY TO REACTION TIME AND MOLECULAR WEIGHT OF OIL

It has been mentioned previously that when an oil is subjected to polymerization there will be long intervals when a plot of the reaction time against the logarithm of the viscosity will yield a substantially straight line. This effect invites speculation, in view of Flory's finding[29] that the viscosity of linear polymers is related in a simple manner to the average molecular weight, and the theoretical relationships developed by Flory[29,30] and others for molecular size distributions in terms of the completeness of reaction of functional groups. Although triglycerides are often trifunctional with respect to polymerization, and capable of

[26] G. A. O'Hare, P. S. Hess, and A. F. Kopacki, J. Am. Oil Chem. Soc., 26, 484–488 (1949).
[27] G. A. O'Hare and W. J. Withrow, Ind. Eng. Chem., 39, 101–104 (1947).
[28] E. H. Hazlehurst, Paint Manuf., 13, 275 (1943).
[29] P. J. Flory, J. Am. Chem. Soc., 62, 1057–1070 (1940).
[30] P. J. Flory, J. Am. Chem. Soc., 58, 1877–1885 (1936); 61, 3334–3340 (1939); 63, 3083–3090 (1941); 64, 2205–2212 (1942); 69, 30–35 (1947); J. Phys. Chem., 46, 132–140 (1942).

forming branched chain structures, it is reasonable to assume that in an oil such as linseed oil the formation of essentially linear polymers would predominate during the earlier stages of the reaction.

Paschke and Wheeler[31] have shown that in the thermal polymerization of normal methyl linoleate, the reaction is first order with respect to the disappearance of the functional $(CH)_2CH_2(CH)_2$ group, so that:

$$t = k \log \frac{1}{1 - p} \tag{1}$$

where p refers to the mol fraction of functional groups reacted at the end of time, t. Where polymerization occurs by the random reaction of func-
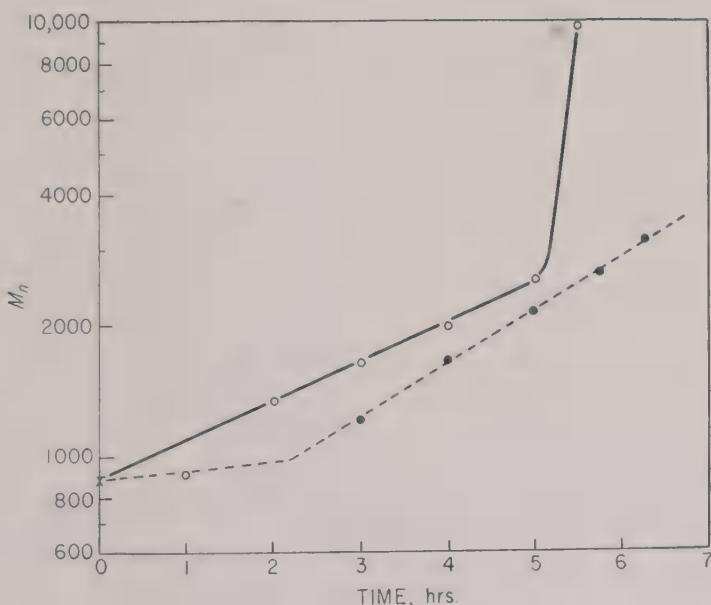
Fig. 161. Mean molecular weight as a function of reaction time in linseed oil subjected to thermal polymerization (solid curve) and oxidation polymerization (broken curve).[26]

tional groups of equal reactivity, with each reaction contributing one additional unit to the multi-unit polymer structure, the *number* average molecular weight, M_n (as determined by ordinary molecular weight measurements), is related to the degree of reaction by an expression of the form:

$$M_n = k' \frac{2}{1 - p} \tag{2}$$

Hence, from Equations (1) and (2):

[31] R. F. Paschke and D. H. Wheeler, *J. Am. Oil Chem. Soc.*, **26**, 278–283 (1949).

$$t = k'' \log M_n \qquad (3)$$

Hence, in the polymerization of a drying oil, if a certain stage is dominated by reaction of a single class of functional groups, a linear relationship might be expected between the reaction time and the logarithm of the viscosity.

Unfortunately, most of the molecular weight determinations in the literature are too inaccurate to shed any light on the validity of the above equation. However, the data of O'Hare et al.[26] (obtained by working with polymerized linseed oil in cyclohexane) may be accepted with some confidence, and these do, in fact, show a linear relationship up to a point where the viscosity curve breaks sharply upward, indicating probably the beginning of a three-dimensional polymer structure (Fig. 161).

Since the logarithm of the number average molecular weight apparently also varies linearly with reaction time, it would appear upon first thought that log viscosity must be directly related to the *number* average molecular weight, rather than to the square root of the *weight* average molecular weight, as was found by Flory[29] for linear polymers. However, the square root of the weight average molecular weight is approximately proportional to the number average molecular weight over limited viscosity ranges, and actually, the results of O'Hare et al. plot about as satisfactorily against the former as they do against the latter (Fig. 162).

Prior to the beginning of gelation, the bodying curve (time *vs.* log viscosity) of linseed oil is usually made up of two separate segments, with a discontinuity at about 1000 centipoises, and similar discontinuities are observed in the bodying curves of other oils (see Figs. 159 and 162). Presumably, each break in the curve represents the beginning of some new mode of molecular aggregation, or the exhaustion of some specific class of functional groups. Shuey[32] has observed that if the viscosity of heat-bodied tung oil is determined at the temperature of the kettle, rather than upon cooled samples, a curve is obtained with three well-defined linear phases. The point corresponding to the end of the first phase is almost exactly that at which the oil begins to become insoluble in acetone, whereas the point corresponding to the end of the second phase is that at which the oil begins to become insoluble in mineral spirits. At 450°F. the viscosities represented by the "acetone" and "mineral spirits" points are respectively about 10 and 25 centipoises.

[32] R. C. Shuey, *Ind. Eng. Chem.*, *32*, 921–930 (1940). See also J. J. Mattiello, editor, *Protective and Decorative Coatings*, Vol. III, Wiley, New York, 1943, pp. 125–129.

As indicated previously, Anderson and Porter[9a] attribute the different slopes of different portions of the curve purely to the existence of several unsaturated fatty acids in the oil, and not to any fundamental difference in successive stages of the reaction.
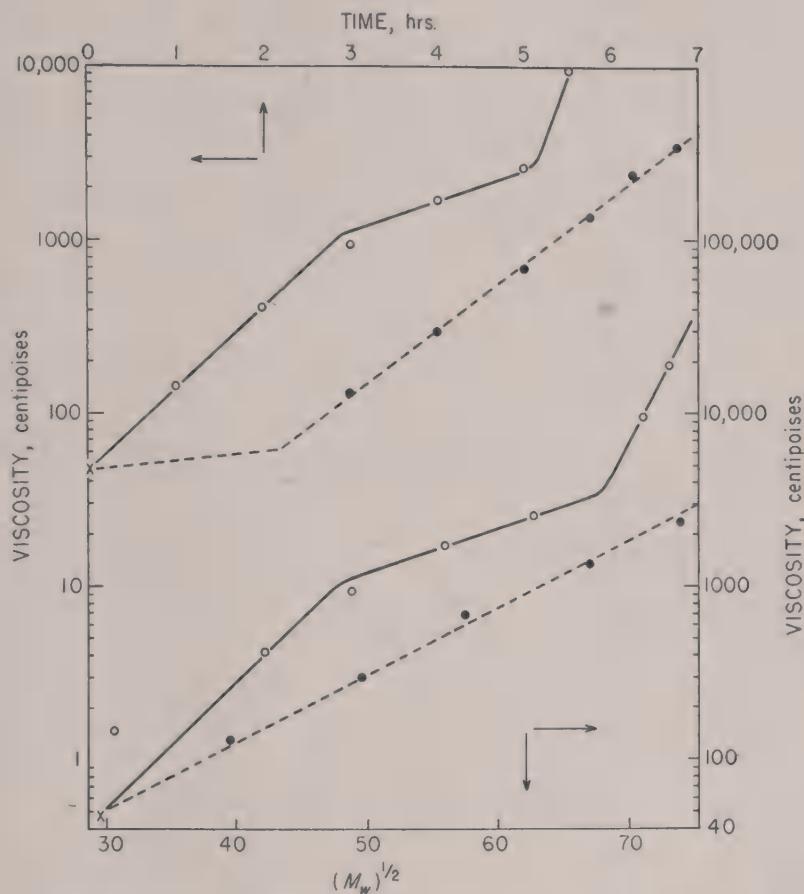
Fig. 162. Viscosity as a function of reaction time and of the weight average molecular weight in linseed oil subjected to thermal polymerization (solid curves) and oxidation polymerization (broken curves).[26]

4. POLYMERIZATION OF FATTY MATERIALS OTHER THAN GLYCERIDES

Dibasic and other polybasic fatty acids, formed by the heat polymerization or carbon-to-carbon linking of fatty acid chains, are of some importance as intermediates for the preparation of high polymeric products[33] (see also page 487), because of their increased functionality as compared with ordinary fatty acids, and also because they are readily re-

[33] See, for example, L. B. Falkenburg, H. M. Teeter, P. S. Skell, and J. C. Cowan. *Oil & Soap*, *22*, 143–150 (1945); J. C. Cowan and H. M. Teeter, *Ind. Eng. Chem.*, *36*, 148–152 (1944); U. S. Pat. 2,477,116 (1949).

moved from unpolymerized fatty acids by distillation, and thus are involved in certain fractionation techniques (Chapter XXI).

Because triglycerides tend to form gels before polymerization is far advanced, oils as such are not suitable raw materials for the manufacture of polybasic acids, and polymerization is preferably carried out on such materials as free fatty acids, soaps, or monoesters. Goebel[24a] has shown that if free fatty acids are reacted under a pressure of 85–400 pounds, in the presence of 1–5% water, the polyethenoid acids in mixed fatty acids can be polymerized without significant decarboxylation. At the high temperatures required to complete the reaction in a reasonable time (about 330–360°C., 626–680°F.) extensive thermal decomposition occurs in the absence of water. The presence of water also favors dimerization at the expense of the formation of higher polymers; in a typical experiment, mixed soybean oil fatty acids produced dibasic acids and tribasic acids in the ratio of 17 to 1, whereas by the polymerization of the corresponding methyl esters the ratio of dibasic acids to tribasic acids was 2.6 to 1. The process is now used commercially.

The production of polymerized monoesters, by thermal reaction under more or less conventional conditions, e.g., at 300°F. or 572°C., has been described by Bradley,[34] and by Cowan and co-workers.[33,35] Percy and Ross[36] have patented a process wherein fatty acids, in the form of sodium soaps, are polymerized at 300–350°F. (572–662°F.).

B. Isomerization[36a]

1. *Cis-Trans* ISOMERIZATION

Although of little or no present commercial importance, the treatment of fats to effect *cis-trans* isomerization is of some interest, as it affords a means of raising the melting point, as well as of improving the resistance of the fat to oxidation, without recourse to hydrogenation.

Conversion of unsaturated acids from the natural *cis*-form to *trans*-forms can be brought about by treatment of fats, according to the common laboratory practice, with nitrous oxide,[37] or with liquid sulfur dioxide at 100–120°C. (212–238°F.)[38] or a small amount (*ca.* 0.1%)

[34] T. F. Bradley and W. B. Johnston, *Ind. Eng. Chem.*, *33*, 86–89 (1941). T. F. Bradley (to American Cyanamid Co.), U. S. Pat. 2,379,413 (1945).
[35] J. C. Cowan and D. H. Wheeler, *J. Am. Chem. Soc.*, *66*, 84–88 (1944). J. C. Cowan and W. C. Ault (to Secretary of Agriculture), U. S. Pat. 2,373,015 (1945). J. C. Cowan and H. M. Teeter (to Secretary of Agriculture), U. S. Pat. 2,384,443 (1945).
[36] J. H. Percy and J. Ross (to Colgate-Palmolive-Peet Co.), U. S. Pat. 2,341,239 (1944).
[36a] For a recent review of the theory and practice of isomerization processes, see J. C. Cowan, *J. Am. Oil Chem. Soc.*, *27*, 492–499 (1950).
[37] W. R. Eipper, U. S. Pat. 2,310,225 (1943).
[38] H. I. Waterman, C. van Vlodrop, and J. Hannewyk, *Research*, *1*, 183–185 (1948); Brit. Pat. 502,390 (1939).

of selenium at 200–210°C. (392–410°F.).[39] The process appears to affect the melting point of fats chiefly through the conversion of oleic acid to elaidic acid; hence its effect is most marked upon fats relatively high in oleic acid. It is well known that *trans*-acids oxidize less readily than the corresponding *cis*-acids, and, according to tests reported by Bertram,[39] the keeping time of fats is extended from two to five times by "elaidination."

It is well established that when oleic acid or other monoethenoid fatty acid or ester is subjected to treatment capable of producing *trans*-isomers, an equilibrium is eventually reached with a ratio of *trans*- to *cis*-forms of 2 to 1. The mechanism of *cis-trans* isomerization has been subjected to a theoretical analysis by Blekkingh,[39a] who has been able to show that this equilibrium would logically result from the fact that geometrical considerations dictate the existence of the *trans*-isomer in four transitional forms, all of which are interconvertible with each other, but only two of which are interconvertible with the *cis*-form, because of steric hindrance. Extension of this reasoning to the case of linoleic acid indicates that at equilibrium the proportion of *trans-trans* to *trans-cis* to *cis-trans*, to *cis-cis* isomers should be 8 to 3 to 3 to 3.

2. ISOMERIZATION TO PRODUCE CONJUGATED ACIDS

The alkali isomerization process for the production of conjugated acid oils from ordinary drying oils grew out of the observation by biochemical workers[40] that there is a tendency for double bonds to undergo a shift in position during the alcoholic saponification of drying oils. The first reported method[41] for producing extensive conjugation in a short time specified treatment with alkali in an alcohol or other high-boiling organic solvent. However, it has subsequently been shown that reaction in an aqueous alkali solution is equally effective, if the operation is carried out at a sufficiently high temperature, and of course under a correspondingly high pressure. Aqueous alkali isomerization has been employed to a limited extent in the commercial manufacture of the isomerized oils during periods when tung oil was in short supply.

The fundamentals of aqueous alkali isomerization are discussed in an article by Bradley and Richardson.[42] These workers found that it was readily possible to produce soybean oil and linseed oil products containing from 30–50% of conjugated fatty acids. The principal factor affect-

[39] S. H. Bertram, *J. Am. Oil Chem. Soc.*, *26*, 83–85 (1949). E. Gordon and M. O. Pailleux, *Bull. mens. ITERG.*, *1948*, No. 8, 31–33.
[39a] J. J. A. Blekkingh, *Bull. soc. chim. France*, *1950*, 278–282.
[40] W. J. Dann and T. Moore, *Biochem. J.*, *27*, 1166–1169 (1933). W. J. Dann, R. G. Booth, J. Golding, and S. K. Kon, *ibid.*, *29*, 138–146 (1935). T. Moore, *ibid.*, *31*, 138–154 (1937).
[41] G. O. Burr (to Regents of the University of Minn.), U. S. Pat. 2,242,230 (1941).
[42] T. F. Bradley and D. Richardson, *Ind. Eng. Chem.*, *34*, 237–242 (1942).

ing the rate of reaction and composition of the reaction product was the temperature; the alkalinity of the reaction mixture and the proportion of water present were found to be only minor factors. There is an optimum reaction time, beyond which there is a decrease in conjugation of the fatty acids.

In commercial practice, soybean oil and linseed oil are said to be first split, and the free acids are subjected to isomerization by caustic soda. The isomerized acids are recovered from their sodium soaps by acidulating the latter, and are then re-esterified with glycerol. The isomerization reaction is said to be carried out in a continuous apparatus; details relative to the proportions of alkali, water, and fatty acids, the reaction time, and the operating temperature, are not available.

It has been found that the amount of conjugation produced during alkali isomerization is not an absolute measure of the drying properties of the isomerized oil, since isomers of a high degree of conjugation but relatively poor drying properties may be produced. A high reaction temperature is said to be particularly favorable to the production of slow-drying isomers. In the case of isomerized linolenic acid, one of the latter isomers appears to be 10:11, 12:13, 14:15-octadecatrienoic acid[43] or "pseudo-eleostearic" acid, which dries at but one-fourth the rate of natural 9:10, 11:12, 13:14-eleostearic acid.[44]

Waterman and co-workers[45] have demonstrated that extensive conjugation is produced in linseed or other nonconjugated drying oils by treatment of the latter with liquid sulfur dioxide. The process is carried out at 180–200°F. (356–392°F.) under a pressure of about 60 atmospheres.

One of the most effective methods for the catalytic isomerization of nonconjugated oils involves use of the special carbon-supported nickel catalyst developed by Kass and co-workers.[46] In typical experiments, treatment of alkali-refined linseed oil in the laboratory with 9% catalyst (containing 19% nickel) at 170–175°C. (338–347°F.) for 3.5 hours was found to produce 25.2% diene conjugation (conjugated acids) and 7.9% triene conjugation, and similar treatment of alkali-refined soybean oil produced 30.4% diene conjugation and 2.7% triene conjugation.[46] Some re-use of the catalyst is feasible, although inactivation is relatively rapid, particularly if the oil contains phosphatides or any considerable amount of free fatty acids. As in the case of alkali-isomerized oils, the drying

[43] J. P. Kass and G. O. Burr, J. Am. Chem. Soc., 61, 3292–3294 (1939).
[44] J. E. Meyers, J. P. Kass, and G. O. Burr, Oil & Soap, 18, 107–109 (1941).
[45] H. I. Waterman, C. van Vlodrop, and M. J. Pfauth, Verfkroniek, 13, 130–136 (1940); Research, 1, 186–192 (1948); Brit. Pat. 544,482 (1942).
[46] S. B. Radlove, H. M. Teeter, W. H. Bond, J. C. Cowan, and J. P. Kass, Ind. Eng. Chem., 38, 997–1002 (1946).

properties of the oil produced by this method are somewhat poorer than might be anticipated from the extensive conjugation obtained, owing to the formation of slow-drying conjugated isomers. Available supplies of tung oil have increased since the process was developed, and it has thus far not attained commercial importance.

Falkenburg et al.[47] found that treatment with 5% anthroquinone at 260–280°C. (500–536°F.) for 2–4 hours produced about 20% total conjugation (largely diene) in either soybean or linseed oil. Turk and co-workers[48] have claimed that certain siliceous materials and alumina and other metallic oxides are effective isomerization catalysts; however, their results appear uncertain, in view of their use of the increase in refractive index as the sole criterion of the amount of conjugation produced. It has been established by a number of workers that conjugation occurs to a minor degree when oils are heated with a great variety of finely divided solid materials, including ordinary bleaching earth.[49]

The use of certain organic and inorganic iodides as conjugation catalysts has been patented by Ralston and Turinsky.[49a] The oxidation-dehydration and halogenation-dehydrohalogenation methods described in a later section produce conjugation as well as additional unsaturation in unsaturated fatty acids.

C. Treatment to Increase Unsaturation

Of various methods and proposed methods for introducing new double bonds and increasing the unsaturation of fats or fatty acids, only the dehydration of castor oil is at present practiced commercially, although certain others are perhaps of potential importance. As explained in an earlier chapter (page 45), the direct catalytic dehydrogenation of oils does not appear a promising approach to the problem of converting non-drying or semidrying oils to drying oils.

1. DEHYDRATION OF CASTOR OIL[49b]

As mentioned previously (page 433), the dehydration of castor oil involves the removal of the hydroxyl group from ricinoleic acid, together with an adjacent hydrogen atom, to yield both 9:10, 11:12 and 9:10, 12:13-octadecadienoic acids. In the original process developed by

[47] L. B. Falkenburg, W. DeJong, D. P. Handke, and S. B. Radlove, J. Am. Oil Chem. Soc., 25, 237–243 (1948).
[48] A. Turk and J. Feldman, Paint, Oil & Chem. Rev., 106, No. 13, 10–11 (1943); A. Turk and P. D. Boone, Oil & Soap, 21, 321–322 (1944).
[49] J. H. Mitchell and H. R. Kraybill, J. Am. Chem. Soc., 64, 988–994 (1942).
[49a] A. W. Ralston and O. Turinsky (to Armour & Co.), U. S. Pats. 2,411,111–113 (1946).
[49b] For a review of modern practice in the commercial dehydration of castor oil, see R. L. Terrill, J. Am. Oil Chem. Soc., 27, 477–481 (1950).

Scheiber,[50] the separated fatty acids of castor oil were dehydrated, and thereafter re-esterified with glycerol. However, most of the oil made at present is produced by direct dehydration of the oil, as first practiced by Ufer,[51] even though it is claimed by Scheiber[52] that dehydration of the free acids produces a much higher yield (at least 70%) of the desired 9:10, 11:12 isomer.

The effective catalysts for dehydration include acid derivatives of sulfuric and phosphoric acids, acidic compounds of tungsten and molybdenum, and certain siliceous materials. Sodium acid sulfate is a particularly suitable catalyst; this and other acid compounds of nonoxidizing mineral acids containing oxygen have been patented by Ufer.[51] Schwarcman[53] claims the use of kieselguhr or other siliceous material carrying a small amount of free sulfuric acid. The use of Japanese acid earth is mentioned by Yamada.[54] Rheineck and Crecelius[17] have patented silicotungstic, phosphotungstic, borotungstic, and molybdophosphotungstic acids as dehydration catalysts. Other proposed catalysts include neutral phosphorus chlorides such as phosphorus oxychloride,[55] neutral alkyl sulfate,[56] a mixture of silica gel, alumina, and thoria,[57] and solid phosphoric acid compositions.[58] Strong sulfuric acid may be used as the catalyst if the oil is treated rapidly, in thin layers.[59]

It is considered by Forbes and Neville,[60] who have made an extensive investigation of different catalysts, that the acidic catalysts probably function according to the following mechanism:
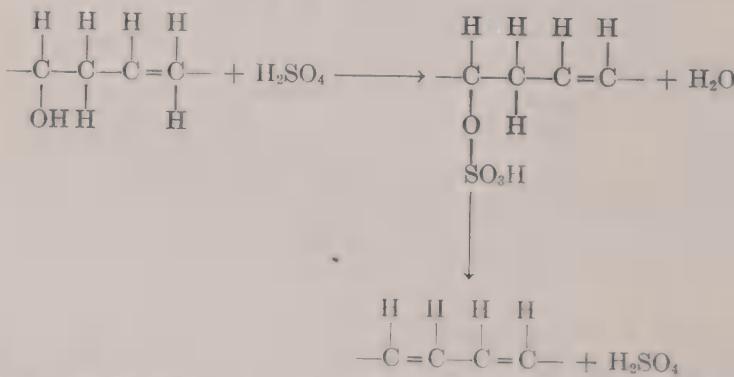
[50] J. Scheiber, Ger. Pat. 513,309 (1930); Brit. Pat. 316,538 (1928); U. S. Pat. 1,942,778 (1934).

[51] H. Ufer (to I. G. Farbenindustrie), Ger. Pats. 529,557 (1931) and 561,290 (1932); U. S. Pat. 1,892,258 (1932).

[52] J. Scheiber, Farbe u. Lack, 55, 147–151 (1949).

[53] A. Schwarcman (to Spencer Kellogg & Sons), U. S. Pat. 2,140,271 (1938).

[54] T. Yamada, J. Soc. Chem. Ind. Japan, Suppl. Bind., 38, 120–123 (1935).

[55] A. Schwarcman (to Spencer Kellogg & Sons), U. S. Pat. 2,330,180 (1944).

[56] A. Schwarcman (to Spencer Kellogg & Sons), U. S. Pat. 2,330,181 (1944).

[57] H. S. Miller (to Air Reduction Co.), U. S. Pat. 2,351,444 (1944).

[58] H. S. Bloch (to Universal Oil Products Co.), U. S. Pat. 2,380,720 (1945).

[59] I. M. Colbeth (to Baker Castor Oil Co.), 2,392,119 (1946). See also S. B. Radlove, W. DeJong, and L. B. Falkenburg, J. Am. Oil Chem. Soc., 25, 268–271 (1948).

[60] W. C. Forbes and H. A. Neville, Ind. Eng. Chem., 32, 555–558 (1940).

The reduction is carried out in closed kettles preferably constructed of stainless steel, which are provided with agitators and some means of producing a reasonably low vacuum. The temperature employed is in the range of about 450° to 475°F; hence a special high-temperature heating system must be provided. The operation is conducted under reduced pressure, to facilitate removal of the evolved water.

Ordinarily less than one per cent of catalyst is used, in the form of a powder. It is important for the catalyst to present a large surface, as the system is heterogeneous; at the conclusion of the reaction the catalyst is filtered out of the cooled oil.

An alternative process for dehydrating castor oil comprises acetylating the free hydroxyl groups and thermally decomposing the acetylated material to drive off acetic acid:[61]

$$
\begin{array}{c}
\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\ \mid \quad\ \mid \quad\ \mid \quad\ \mid \\
-\text{C}-\text{C}-\text{C}=\text{C}- \ +\ \text{CH}_3\text{COOH} \longrightarrow \\
\ \mid \quad\ \mid \\
\text{HO} \quad \text{H}
\end{array}
\qquad
\begin{array}{c}
\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\ \mid \quad\ \mid \quad\ \mid \quad\ \mid \\
-\text{C}-\text{C}-\text{C}=\text{C} \ +\ \text{H}_2\text{O} \\
\ \mid \quad\ \mid \\
\text{CH}_3\text{COO} \quad \text{H}
\end{array}
$$

$$
\downarrow
$$

$$
\begin{array}{c}
\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\
\ \mid \quad\ \mid \quad\ \mid \quad\ \mid \\
-\text{C}=\text{C}-\text{C}=\text{C}- \ +\ \text{CH}_3\text{COOH}
\end{array}
$$
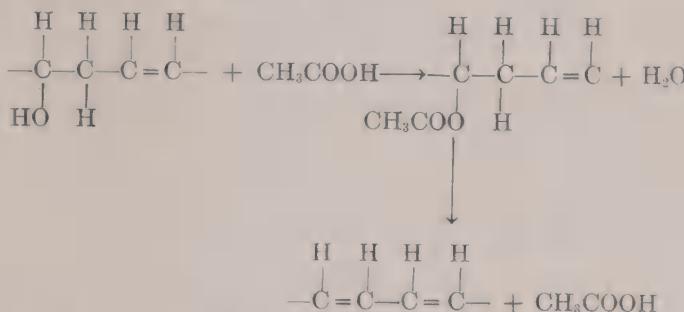
A detailed study of the reaction has been made by Grummitt and Fleming,[62] who found that the decomposition of the acetylated oil was a first-order reaction, rather highly sensitive to temperature in the range 295–340°C. (563–644°F.) (the calculated energy of activation was 44.5 kcal.). Although temperatures of 250–300°C. (482–572°F.) are mentioned in the patents covering the process,[61] Grummitt and Fleming recommend a higher temperature (320–340°C.) and a short reaction time if polymerization of the oil is to be minimized, with a packed and heated column under reduced pressure being used as a reactor. By continuously removing water of esterification by distillation or other means, they found it feasible to substitute acetic acid for acetic anhydride as the acetylating agent. For acetylation, p-toluenesulfonic acid was found to be an effective catalyst, easily removable by clay treatment of the product at the conclusion of the reaction. Of a number of substances tested as catalysts for the thermal decomposition step, only p-toluenesulfonyl chloride was effective without discoloring the oil.

Patents have been issued covering processes similar to the above in which the hydroxyl groups of ricinoleic acid are esterified with phthalic

[61] J. S. Brod, U. S. Pat. 2,212,385 (1940); F. G. Nessler and E. F. R. Schuelke (to Sherwin-Williams Co.), Can. Pat. 428,728 (1945).
[62] O. Grummitt and H. Fleming, *Ind. Eng. Chem.*, *37*, 485–491 (1945).

acid[63] and octadecadienoic or other long-chain unsaturated fatty acids.

It has been shown by Priest and Von Mikusch[65] that ordinary 9:10, 12:13-linoleic or octadecadienoic acid is produced by dehydration in considerably greater quantity than the more desirable 9:10, 11:12 conjugated octadecadienoic acid (page 433). It is claimed that the oil, Dienol, produced by the Swiss Münzel process[66] contains only 9:10, 11:12 acid, but this claim has not been confirmed by workers in the United States.[65]

2. OXIDATION-DEHYDRATION AND HALOGENATION-DEHYDROHALOGENATION METHODS

New double bonds may be introduced into unsaturated fatty acids or glycerides in conjugated positions by oxidation followed by dehydration or halogenation followed by the removal of hydrogen halide. The accompanying simplified equations (1)–(3) will serve to show the essential reactions involved.

Improvement in the drying properties of cottonseed and soybean oils following chlorination and dehydrochlorination was reported by Gardner and Bielouss[67] as early as 1922. Treatment of a specially dehydrated castor oil with hypochlorus acid, followed by dehydration and dehydrochlorination (see reaction 3 above), is said to have been used in Switzerland[68] for the commercial production of a synthetic oil, Trienol, capable of drying and polymerizing even more rapidly than natural tung oil. However, authentic samples of such an oil have apparently not materialized in this country.

Patents have been issued to Boone[69] and to Colbeth[70] covering oxidation-dehydration procedures. Turk and co-workers[71] have reported experiments in which oils were oxidized with selenium dioxide as a preliminary to dehydration.

Actually, treatment of oils by any of the methods outlined is not nearly as simple as indicated by the equations, because of the difficulty of inducing oxidation or halogenation at the desired points, without the occurrence of undesirable side reactions, and because of the difficulty of

[63] R. T. Ubben and J. R. Price (to Armstrong Paint & Varnish Works), U. S. Pat. 2,246,768 (1941).

[64] F. G. Nessler (to Sherwin-Williams Co.), U. S. Pat. 2,336,186 (1943).

[65] G. W. Priest and J. P. Von Mikusch, *Ind. Eng. Chem.*, *32*, 1314–1319 (1940).

[66] See F. Münzel, Swiss Pat. 193.931 (1938). Also A. V. Blom in *Varnish Making*, Chemical Pub. Co., New York, 1940, pp. 31–39.

[67] H. A. Gardner and E. Bielouss, *J. Ind. Eng. Chem.*, *14*, 619–621 (1922).

[68] See A. V. Blom in *Varnish Making*, Chemical Pub. Co., New York, 1940, pp 31–39.

[69] P. D. Boone, U. S. Pat. 2,308,152 (1943).

[70] I. M. Colbeth, U. S. Pat. 2,388,122 (1945).

[71] A. Turk, J. W. Dawson, and S. Soloway, *Am. Paint J.*, *28*, No. 9, 9, 16, 18, 20 (1943).

$$-\overset{\underset{|}{H}}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{\underset{|}{H}}{C}-\overset{\underset{|}{H}}{C}-\overset{\underset{|}{H}}{C}- + O \longrightarrow -\overset{\underset{|}{H}}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{\underset{|}{H}}{\underset{OH}{C}}-\overset{\underset{|}{H}}{\underset{H}{C}}-\overset{\underset{|}{H}}{\underset{H}{C}}- \longrightarrow$$

$$-\overset{\underset{|}{H}}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{H}{C}=\overset{H}{C}-\overset{\underset{|}{H}}{\underset{H}{C}}- + H_2O \qquad (1)$$

$$-\overset{\underset{|}{H}}{\underset{H}{C}}-\overset{\underset{|}{H}}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{\underset{|}{H}}{\underset{H}{C}}-\overset{\underset{|}{H}}{\underset{H}{C}}- + Cl_2$$

$$-\overset{\underset{|}{H}}{\underset{H}{C}}-\overset{\underset{|}{H}}{\underset{H}{C}}-\overset{\underset{|}{H}}{\underset{Cl}{C}}-\overset{\underset{|}{H}}{\underset{Cl}{C}}-\overset{\underset{|}{H}}{\underset{H}{C}}-\overset{\underset{|}{H}}{\underset{H}{C}}-$$

$$-\overset{\underset{|}{H}}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{H}{C}=\overset{H}{C}-\overset{\underset{|}{H}}{\underset{H}{C}}- + 2\,HCl \qquad (2a)$$

$$(+ 2\,NaOH)$$

$$-\overset{\underset{|}{H}}{\underset{H}{C}}-\overset{\underset{|}{H}}{\underset{H}{C}}-\overset{\underset{|}{H}}{\underset{OH}{C}}-\overset{\underset{|}{H}}{\underset{OH}{C}}-\overset{\underset{|}{H}}{\underset{H}{C}}-\overset{\underset{|}{H}}{\underset{H}{C}}- + 2\,NaCl$$

$$-\overset{\underset{|}{H}}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{H}{C}=\overset{H}{C}-\overset{\underset{|}{H}}{\underset{H}{C}}- + 2\,H_2O \qquad (2b)$$

$$-\overset{\underset{|}{H}}{\underset{H}{C}}-\overset{\underset{|}{H}}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{\underset{|}{H}}{\underset{H}{C}}-\overset{\underset{|}{H}}{\underset{H}{C}}- + HOCl \longrightarrow -\overset{\underset{|}{H}}{\underset{H}{C}}-\overset{\underset{|}{H}}{\underset{H}{C}}-\overset{\underset{|}{H}}{\underset{OH}{C}}-\overset{\underset{|}{H}}{\underset{Cl}{C}}-\overset{\underset{|}{H}}{\underset{H}{C}}-\overset{\underset{|}{H}}{\underset{H}{C}}- \longrightarrow$$

$$-\overset{\underset{|}{H}}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{H}{C}=\overset{H}{C}-\overset{\underset{|}{H}}{\underset{H}{C}}- + H_2O + HCl \qquad (3)$$
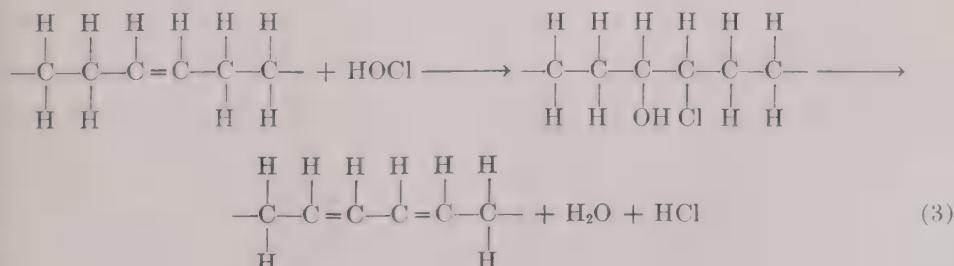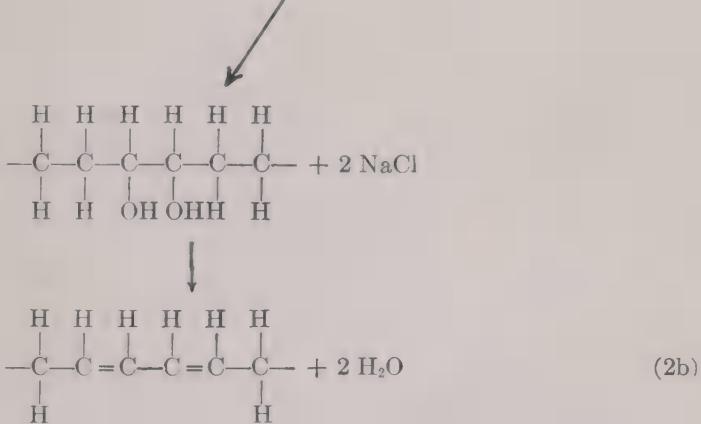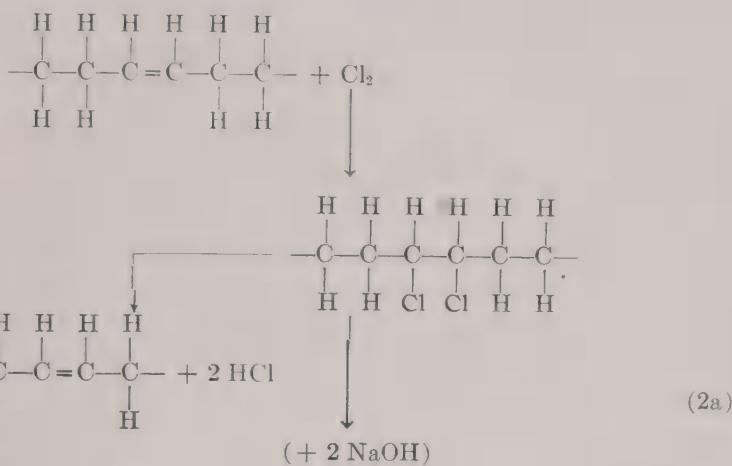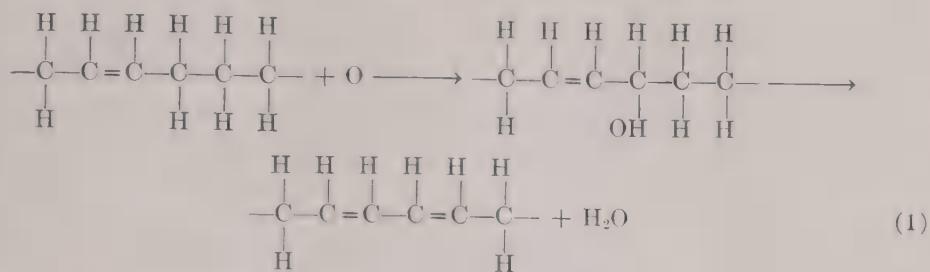
removing halogen completely in the second step of dehydrohalogenation
Recent and only partial successful experiments in the chlorination an
dehydrochlorination of fatty acids and their esters have been reported b
Van Atta et al.[72] and Teeter et al.[73]

[72] G. R. Van Atta, D. F. Houston, and W. C. Dietrich, *J. Am. Oil Chem. Soc*
24, 149–155, 209–212 (1947).
[73] H. M. Teeter and J. E. Jackson, *J. Am. Oil Chem. Soc.*, *26*, 535–540 (1949)
H. M. Teeter, R. C. Bachmann, E. W. Bell, and J. C. Cowan, *Ind. Eng. Chem.*, *4*.
849–852 (1949).

SOLIDIFICATION, HOMOGENIZATION, AND EMULSIFICATION

A. Introduction

The processes of solidification, homogenization, and emulsification are classified together because they have a common object, as applied to fatty materials. The purpose of each is to produce a two-phase system, with a high degree of interdispersion of the two phases. In the case of solidification, the two phases are respectively the solid and liquid forms of a fat or similar material. In the case of emulsification, the two phases are a liquid fat, and water or an aqueous solution. The term "homogenization" is applied to treatment designed to produce a further degree of dispersion in a preformed system comprising either solid and liquid fats or fatty and aqueous phases.

All fat products which are solidified in the course of their manufacture are actually *plastic solids* except at extremely low temperatures, *i.e.*, they consist of an intimate mixture of liquid and very small solid particles. The liquid is retained in the framework of solids by capillarity, and the tendency of the solid particles to interlock and cohere gives the material the resistance to limited deforming stresses which is characteristic of plastic systems. Obviously the plastic properties of such a material are very largely dependent upon such factors as the relative proportions of solids and liquids, the size and size distribution of the solid particles, the shape of the particles, and their rigidity and degree of mutual attraction. As some of these factors are influenced by the manner in which solidification is conducted, some care is required in this operation to obtain desirable properties in the solidified product.

The technical solidification of fats, soaps, etc. is complicated by the fact that these materials are polymorphic, *i.e.*, they are capable of existing in different crystal modifications, according to the conditions under which they are solidified. Different solid modifications of the same material are different in melting point and other physical characteristics; hence polymorphism alone may account for wide variations in the properties of a single plastic product solidified by different methods.

The consistency of an emulsion, as well as its stability, depends to a

considerable degree upon the extent to which the discontinuous liquid phase is dispersed.

B. Solidification and Homogenization of Plastic Products[1]

1. PLASTICIZING OF LARD AND SHORTENINGS

The characteristic structure of commercially solidified lard and shortenings has been shown in Figure 15 (Chap. VIII). These fats consist of a mass of small needlelike crystals enclosing liquid oil. The crystals of lard (and hydrogenated lard) are invariably much larger than those of shortenings, but appear to be of the same shape. In the solidification of these fats the finest possible crystal structure is desired, to render the product smooth in appearance and firm in consistency; hence the crystals are formed by chilling the fat very rapidly. It is also customary to whip into lard about 6–8%, or into shortening about 10–12% of its own volume of air, in the form of very small bubbles, most of which are about 10–50 microns in diameter. These bubbles are permanently retained by the plastic fat, and serve to give it a white and opaque, rather than a translucent appearance.

The oldest apparatus for the solidification of lard and shortenings is the chilling roll, which is similar in both appearance and operation to the roll described previously for the solidification of soap flakes. It consists of a large, hollow iron cylinder with a surface machined and ground smooth to true cylindrical form. A roll of common size is 4 feet in diameter and 9 feet long, and has a capacity in the neighborhood of 10,000 pounds per hour.

The roll is internally refrigerated by the direct expansion of ammonia or other refrigerant, or in some cases by the circulation of cold brine. Turning slowly (6–9 r.p.m.) on its longitudinal and horizontal axis, the roll picks up on its surface a thin coating of the molten fat from a trough formed by a wooden frame bearing against the surface and running its full length. The trough is supplied by lines from the storage tanks of liquefied fat. The temperature of the fat supplied to the roll is somewhat variable, but is in no case very far above the solidification point of the fat. In some installations the thickness of the fat coating depends simply upon the viscosity of the molten fat and the speed of the roll. In others, an adjustable blade is set close to the roll just above the trough, to scrape off and return to the trough any fat in excess of a definite film thickness.

The coating of fat picked up from the trough is carried up over the roll, and having solidified, is taken off by a scraper blade bearing against the

[1] See E. M. James in *Cottonseed and Cottonseed Products*, A. E. Bailey, ed., Interscience, New York, 1948, pp. 725–730; J. E. Slaughter, Jr., and C. E. McMichael, *J. Am. Oil Chem. Soc.*, 26, 623–628 (1949).

roll near the bottom of the feed trough. The solidified fat, in the form of a thin, translucent, plastic sheet, drops into a "picker box," which consists of an open trough bearing a screw conveyor. The flights of the conveyor are interspersed with blades which, revolving in the partially filled trough, beat air into the fat. The amount of air incorporated is somewhat roughly controlled by varying the amount of fat maintained in the picker box. The temperature of the fat from the roll will vary according to the nature of the fat and the particular method of operating the roll, but will ordinarily be in the neighborhood of 55–65°F. The temperature is inclined to rise somewhat in the picker box and in the lines from the picker box, since there is delayed crystallization, with consequent evolution of heat, for some time after the fat is first chilled.

From the picker box the fat is fed to a high-pressure steam pump, which raises the pressure on the lines leading to the filling machine to about 300 to 500 pounds per square inch. The fat entering the high-pressure system is by no means thoroughly homogenized, and if it is filled at once it will be lacking in smoothness and whiteness, and contain many small, translucent lumps devoid of air. Homogenization is accomplished by forcing the fat, under this high pressure, through various devices set in the lines to the fillers. These may consist of orifices, slots, screens, valves, etc., but all represent some form of constriction in the line, which applies to the moving material intense shearing forces, and thus breaks up any aggregates of material. In some systems more than one pump is employed to enable homogenization to be carried out in more stages than is possible with a single pump.

After the final stage of homogenization, the product is discharged directly into packages, automatic filling machines being usually used for the smaller packages, while the larger ones are filled by hand.

The roll system of solidification, while simple, and requiring the use of relatively inexpensive equipment, is unsatisfactory in some respects. The refrigerated surface of the roll is exposed to the atmosphere, and this causes some loss of refrigeration. Any moisture in the atmosphere is free to condense on the surface of the roll, and thence be transferred to the solidified fat. In humid weather this may be a source of considerable annoyance. Probably the greatest disadvantage of the chill roll, however, is the difficulty of controlling it to obtain a uniform product. Particular difficulty is experienced in maintaining a constant incorporation of air into the fat. This not only makes the product variable in appearance, but also occasions difficulty in filling the packages to a definite weight, since all automatic package-filling equipment operates on a volumetric basis.

The disadvantages of chill rolls mentioned above are avoided in the newer Votator closed chilling machines, which have replaced rolls altogether in most modern plants. In these solidification takes place in small,

externally refrigerated cylinders through which the fat is continuously pumped. They are equipped with sharp, fast-revolving scraper blades, which are caused to bear lightly against the cylinder walls by centrifugal force and the resistance to rotation offered by the fat. Their continual scraping action prevents the formation of a stagnant film on the heat transfer surfaces, and results in a very high rate of heat transfer (of the order of 300 Btu. per hour per square foot per °F.); hence the units are very compact.[2]   Thus a Votator chiller handling 10,000 pounds of lard or

(1) PRODUCT CONNECTIONS
(2) PRODUCT CHAMBER
(3) HEAT TRANSFER MEDIUM CONNECTIONS
(4) HEAT TRANSFER MEDIUM CHAMBER
(5) HEAT TRANSFER TUBE
(6) MUTATOR SHAFT
(7) SCRAPER BLADES
(8) INSULATION
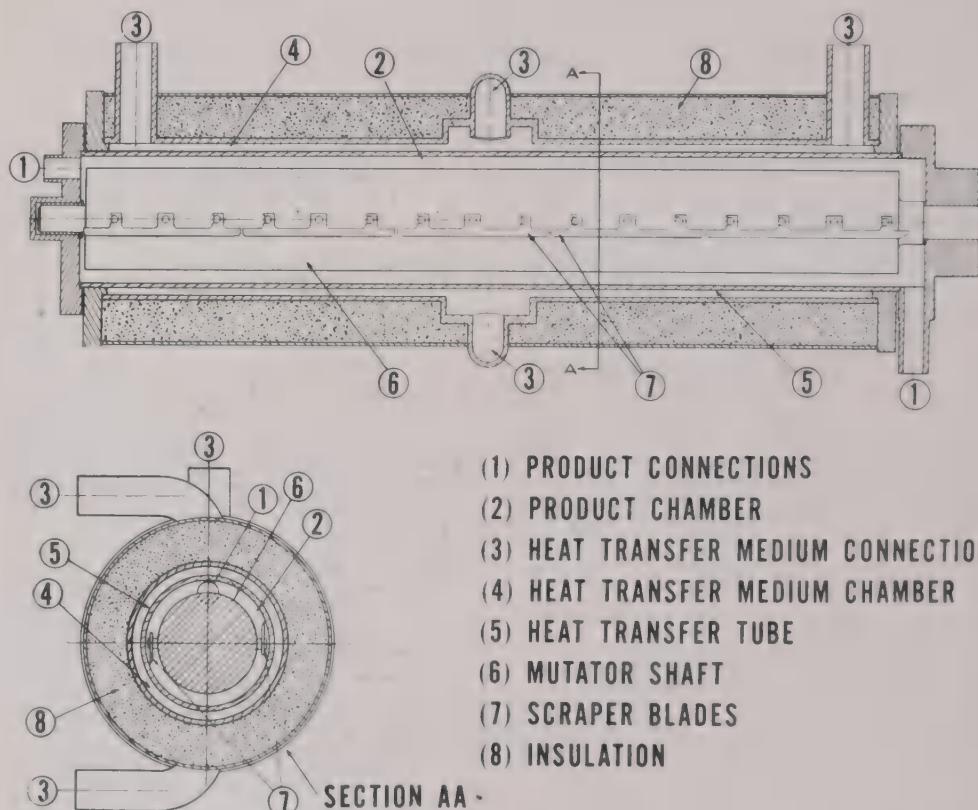
SECTION AA -

Fig. 163. Cylinder of Votator chilling machine, cross and longitudinal sections (courtesy of *The Girdler Corp.*).

shortening per hour requires but 18 square feet of heat-transfer surface, as compared with about 110 square feet for a chill roll of equivalent capacity. Other standard units have capacities of 5000 and 3000 pounds per hour. As shown in Figure 163, the shaft carrying the scraper blades is of large diameter, so the fat must pass through a rather narrow annular space between the shaft and the cylinder walls. The latter are generally cooled by the direct expansion of ammonia.

[2] For a discussion of heat transfer in the Votator machine, see H. G. Houlton, *Ind. Eng. Chem.*, **36**, 522–528 (1944).

The following describes the complete sequence of operations in the solidification of lard or shortening. From holding tanks the melted fat is fed to a small float-controlled supply tank, from which it is picked up by a gear pump and forced first, under pressure, through a coil-type cooler, where its temperature is reduced to 115–120°F., and then through one or more chilling cylinders designated as "A" units. Air or nitrogen to be dispersed in the product is admitted in controlled flow into the suction of the pump. Within a period of 9–18 seconds, the fat is chilled to 60–65°F. It leaves the chilling cylinders in a supercooled and highly
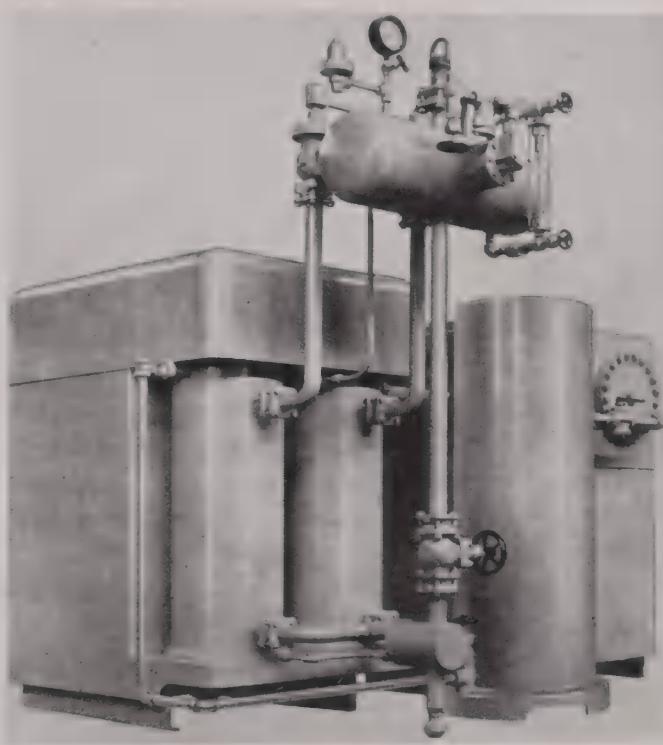
Fig. 164. Votator machine for chilling and plasticizing shortening at the rate of 10.000 pounds per hour (courtesy *The Girdler Corp.*).

fluid condition, but with nuclei established for the formation of a very fine crystal structure. Crystallization is substantially completed in closed cylinders somewhat larger than the chilling cylinders, known as "B" units, which are equipped with rotating shafts set with projecting fingers. These fingers are placed on the shaft in a spiral pattern, to produce a helical movement of the fat through the cylinder, and they intermesh with similar stationary fingers projecting from the cylinder wall. The "B" unit is not jacketed or cooled—its function is merely to main-

tain the fat in a state of uniform agitation—while crystallization proceeds. If fat is filled directly into containers from the chilling cylinders, and allowed to crystallize therein in a static condition, it will be of poor texture and excessively hard, possibly through crystals growing together to form a more or less continuous lattice throughout the fat. In the "B" unit the temperature of the fat rises several degrees, e.g., to 75–85°F., through liberation of its heat of crystallization. Ordinarily, large lard units are equipped with one "B" unit, whereas shortening, which requires more working, is processed through two units.

A second pump takes the fat from the "B" units and forces it, at 250–400 pounds pressure, through a homogenizing valve, and thence to the package fillers. The design and operation of the different types of automatic packaging equipment for shortening and lard are described by James and by Slaughter and McMichael.[1]   Ordinary lard and the lower grades of shortening are packed for retail sale in one-, and to some extent, in two-, and four-pound cartons. Bland-type lard products and shortenings of the all-hydrogenated type are packed in one- and three-pound sealed tins. Some brands are sealed under nitrogen. The common packages for commercial users are tinplate cans of 50 and 100 pounds capacity, and steel drums with removable heads holding approximately 400 pounds. After filling, shortening must be tempered for 24–72 hours, depending upon the size of the container, usually at 80–85°F., to develop optimum consistency and creaming characteristics (see page 301).

2. Solidification of Margarine

While methods for the solidification of margarine are in most respects similar to those employed for the solidification of shortening, certain complications are introduced by the circumstance that margarine is not a pure fat, but an emulsion consisting of about 80% plastic fat and 20% milk and salt.

Three different processes are used for solidifying this product. In these the emulsion of oil and aqueous liquid is respectively sprayed into cold water, solidified on the surface of a chilling roll, and solidified in the closed Votator chilling apparatus. The three processes were developed in the order mentioned. At present the cold water method is very nearly obsolete, at least in the United States, whereas the roll method has been largely supplanted by solidification in the closed chilling machine. As the two older methods are discussed in some detail in another chapter devoted to margarine manufacture in general, this section will be devoted to a further description of the last-mentioned process.

The apparatus used for the solidification of margarine is, in general, similar to that used for lard or shortening. Standard units include a

three-cylinder "A" unit machine with a rated capacity of 4500 pounds of product per hour and a single-cylinder "A" unit machine with a capacity of 1500 pounds per hour. Whereas in shortening manufacture a maximum working and softening of the product in the "B" unit is desired, this is not the case in the solidification of margarine, which must remain reasonably firm if it is to be formed into prints that can be handled and wrapped by automatic machines. Consequently, in the margarine machine agitators are omitted in the "B" units, which consist simply of cylindrical tubes through which the partially solidified fat is forced in a relatively quiescent state by the pressure of the charge pump. By making them of sectional construction, the length (and holding time) may be adjusted to the setting characteristics of the particular fat processed. In the "A" unit the emulsion is chilled to a somewhat lower temperature than is shortening or lard, i.e., to 45–55°F.

According to the most common practice, all constituents of the margarine are simply mixed together to form a coarse emulsion, which is fed at a temperature slightly above the melting point of the fat, e.g., 100°F., to the chilling machine. However, some processors employ proportioning pumps for the oily and aqueous portions of the mixture, and feed a portion of the milk into a blender placed between the "A" and "B" units. This produces a coarser or less "tight" emulsion in the finished product, which is believed to enable the aqueous phase to contribute a more pronounced flavor when the margarine melts in the mouth.[3]

The solidified product issuing from the "B" unit is formed directly into prints, which are wrapped, overwrapped, and cartoned, all by automatic machinery. A common type of print molder has an open hopper into which the fat from the "B" unit is extruded through a perforated plate. Screws at the bottom of the hopper propel the material into a printing head, from which prints are discharged into a wrapping machine.

Virtually all margarine is sold in one-pound packages, which contain either a single print, or frequently, in the case of colored margarine, four one-quarter pound prints. Uncolored print margarine is packaged with a separate small envelope of oil-soluble dye which must be mixed in by the consumer. Within recent years, the so-called Peters bag[4] has become a highly popular package for the uncolored product. It consists of a sealed envelope or bag of pliant plastic material, with the dye contained in a capsule affixed to the interior bag wall. By pinching the capsule with the fingers, it may be broken, after which the product may be uniformly colored by kneading and manipulating the bag before it is opened. Much of the inconvenience of coloring the product is thus avoided. Bag margarine is filled similarly to shortening, with the use of a shortening-type

[3] See A. A. Robinson, *Oil & Soap.* *15.* 203–206 (1938).
[4] L. Peters. U. S. Pat. 2,347,640 (1944).

"B" unit, and must be somewhat softer than ordinary margarine. For the manufacture of bag margarine, a common practice is to blend ordinary margarine oil with a minor proportion of refined and deodorized liquid oil. With the recent removal of Federal restrictions on the sale of colored margarine, the bag may be expected to find more restricted use.

3. Solidification of Soap Products

Since the commercial solidification of soaps has been described in Chapter XX, it will be unnecessary to discuss the subject in any detail here. It may be mentioned, however, that while continuous solidification of certain bar soaps has been adopted by some of the large manufacturers, the continuous process has as yet by no means assumed the importance in the soap industry that it has in the edible fat industry. The continuous closed chilling machines used for processing soaps are similar in principle to those used for shortening and margarine, but have special construction features necessitated by the heavier body of the material handled, and a tendency of the soap to build up on unscraped surfaces within the machine.

As mentioned previously, the continuous solidification of soaps is greatly complicated by the polymorphism of these materials.

The commercial solidification of lubricating greases stiffened by soaps of various metals has been discussed in Chapter XIII.

C. Emulsification[5]

The dispersion of one liquid in another, to form an emulsion, is not very different in principle from the dispersion of a solid in a liquid. As the liquid particles comprising the discontinuous phase become smaller in size they tend to behave more and more like solids, being circumscribed by surface tension forces which maintain them in a relatively rigid spherical form, and strongly resist deforming stress tending to cause further subdivision. Because of the strength of surface tension in droplets of small dimensions, and the impossibility of applying force to overcome surface tension without wasting considerable energy in merely shearing the continuous phase, the power requirements for producing very fine emulsions are considerable.

The type of emulsifying machine most commonly employed consists of some arrangement of mixer blades partially immersed and revolving rapidly in the liquids to be emulsified. Often the operation is carried out in batches, and one of the liquids is slowly added to the batch while the

[5] For a detailed discussion of methods and machines for forming technical emulsions, see Assoc. Leather Trades Chemists, *Emulsion Technology*. Chemical Pub. Co., New York, 1944.

latter is continually agitated. In this form of emulsifier the kinetic energy of the blades striking the liquids is utilized to cause subdivision of one of the liquids and produce an emulsion. Although this arrangement does not produce the finest emulsions, it is simple, relatively efficient from the standpoint of power consumption, and entirely satisfactory for many purposes. A common example of emulsifier of this type is the ordinary household egg beater. Machines utilizing this principle are extensively used in commercial bakeries and mayonnaise plants. They are in general best adapted to the discontinuous preparation of material in relatively small batches.

Homogenizing valves are used to produce fine emulsions, as well as to break up aggregates of material in plastic fats. These valves are in effect spring-loaded constrictions or orifices. They generate intense shearing forces in the liquid mixture as it is forced past them under high pressure. These forces serve to break up the disperse phase more thoroughly than is possible in emulsifiers of the beater type. The pumps used in connection with homogenizing valves are usually of the reciprocating type, and are built with a multiplicity of cylinders to deliver a steady flow of material to the valves. They often produce pressure in excess of 1000 pounds per square inch. Ordinarily a coarse emulsion is first produced by ordinary mixing of the two liquids, and the coarse emulsion is then further homogenized. Homogenizing valves are particularly used for producing fine emulsions in ice cream mixes, condensed milk, fluid milk, and other dairy products. Homogenization by this method is of course continuous.

The finest emulsions are produced in so-called colloid mills, which depend for their effect on the intense shear developed between accurately ground, fast revolving rotors, or rotors and stators operating with a clearance of the order of 0.001 inch, or less.

Colloid mills are used for the processing of mayonnaise and for the preparation of very fine emulsions of a specialty nature.

Y

Z

SUBJECT INDEX

A

Accelerated oxidation tests. See *Stability, tests for*.
Acetylmethylcarbinol, 263
Acetyl value, 72
Acid chlorides, 44
Acid refining. See *Refining*.
Acid value, 42
Acidolysis, 813–815
Acidulation of soapstock, 647
Active methylene group, 9, 55, 57, 250–252, 706
Active oxygen method, 64
Active spots, 710
Activity coefficient, oil solvent mixtures, 604
Adenanthera pavonina, 11
Adducts, maleic anhydride, 421, 440
    urea, 892
Adhesion, work of, 334
Adhesion tension, 334
Aeration tests, 64
Aerosols, 396
Air, absorption by shortenings, 296–298
    blowing of drying oils, 903–906
    content of lard and shortenings, 920
    incorporation in cake mixing, 300–302
Alcohols, fatty, lead soap process for, 763
    by hydrogenation, 762, 763
    occurrence in oils, 28
    by sodium reduction, 43, 764, 765
    use in manufacture of surface-active agents, 388, 393
Alcoholysis of fat, with lower alcohols, 815–818
    with polyhydric alcohols, 818–826
Aldehydes, in oxidized fats, 49, 51, 52
    preparation from fatty acids, 72, 73
Aleurites fordii, 177
Aleurites molucanna, 175
Aleurites montana, 177
Alkali refining. See *Refining*.
Alkyd ratio, 444
Alkyd resins. See also *Resins*.
    manufacture, 465–469
    structure, 443, 467, 468
    use of, 443–445
Alkyl amide sulfates, 394, 395
Alkyl amide sulfonates, 396
Alkyl aryl sulfonates, 385, 396, 397
Alkyl ester sulfates, 382, 394

Alkyl ester sulfonates, 395, 396
Alkyl sulfates, 382, 393, 394
Alkyl sulfonates, 395
Allis-Chalmers extractor, 598
Almond oil, 166
Amides, fatty, 43
Amines, fatty, 44, 765, 766
Amine soaps, 348
Anderson extractor, 598
Animal fats, 122, 142–150. See also *Lard, Tallow*.
Antifoaming agents, 335, 336, 401, 407
Antioxidants, 30–34, 54, 59–64
    inactivation of, 305–309
    recovery from oils, 893–895
    theory of, 60–62
    use in lard, 228–232
Antiskinning agents, 450
Antispattering agents, 283, 284
A. O. M. See *Active oxygen method*.
Apricot kernel oil, 166
Arachidic acid, 10, 11, 41, 46
Arachidonic acid, 16, 17, 41, 46
Arachis hypogaea, 153
Arachis oil. See *Peanut oil*.
Araliaceae, 13
Armacs, 504
Armeens, 504
Armids, 504
Arneels, 504
Arquads, 398
Ascorbic acid esters, 66, 230
Aspergillus glaucus, 513
Astrocaryum murumuru, 138
Astrocaryum tucuma, 138
Attalea cohune, 138
Azelaic acid, 49, 504

B

Babassu oil, 137, 138
Bactericides and bacteriostatic agents, 379, 405
Bacteriology, of butter and margarine cultures, 260–264
    of margarine, 276, 277
Baked goods, 292–326
    consumption of fats in, 292, 293
    materials used in, 293
    percentages of fat in, 292
    production and consumption of, 293

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